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THE PAINTER'S LABORATORY GUIDE.

THE

PAINTER'S LABORATORY GUIDE:

A HANDBOOK ON PAINTS, COLOURS, AND VARNISHES FOR STUDENTS.

BY

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PREFACE.

The experience gained by many years' work as a Teacher of Classes in Painters' Colours, Oils, and Varnishes at the Municipal School of Technology, Manchester, in connection with the City and Guilds of London Institute, convinced me that students would welcome a Laboratory Text-book dealing with the same subject. The publishers of my *Manual of Painters' Colours, Oils, and Varnishes* have also been frequently asked for such a book, and they have in consequence entrusted me with its preparation, which I the more readily undertook in view of the teaching experience above referred to.

In writing this book the requirements of students who can attend practical courses in the subject at some Technical School or College, as well as those of students who, although unable to attend such courses, desire the benefits obtainable from a course of experimental work, have been steadily kept in view. In connection with the Sections on Pigment Making I have described a series of simple experiments, which include (1) the chemical principles on which the preparation of the pigment is based, and (2) its chemical properties; and have added short notes on its manufacture on a large scale. Some pigments, such as ultramarine, yellow ochre, barytes, &c., cannot

(for obvious reasons) be made in the laboratory, but experiments are given which show their principal properties and the methods of testing them. In the Section on Lakes I have given special attention to the preparation of lakes from coal-tar dyes, owing to their rapidly increasing importance.

The experiments with oils are such as can be carried out by students whose time for experimental work is perhaps limited.

By the permission of Messrs. Charles Griffin & Co. I have been enabled to make use of several illustrations from Chemical Wōrks which they publish, viz.:—Figs. 3, 4, 6, 7, 10, 12, from Prof. A. H. Sexton's *Qualitative Analysis*, Fig. 8 from the same writer's *Quantitative Analysis;* Figs. 13 and 14 from Messrs. Dupré & Hake's *Inorganic Chemistry;* and Figs. 19 and 21 from Dr. Boverton Redwood's *Petroleum.* The remaining illustrations have been drawn specially for this work.

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THE

PAINTER'S LABORATORY GUIDE.

CHAPTER I.

PAINTS, PIGMENTS, AND VARNISHES.

Paint.—One of the features of the last hundred years has been the increasing use of paints and varnishes for painting and decorating houses, buildings, and engineering constructions of all kinds. Such application of paint and varnish has a twofold object—(1) To protect the structures from the destructive effects of weather; (2) to decorate them.

Most building materials are more or less acted on by light, air, rain, snow, sleet, and the other influences denoted by the term "weather." The metals generally used are oxidised or corroded; the woods and wood substitutes are liable to decay; stones slowly crumble down and become disintegrated; while very few substances remain undeteriorated for many centuries or thousands of years. By covering them with a coating of paint and varnish this weathering action is moderated or almost entirely checked, and, consequently, the materials retain their soundness and strength for a much longer time when so protected than when not protected. The scope of this book is restricted to the protective action of paints and varnishes, and does not extend to the protection of the materials indicated by other means, nor to a discussion of the processes by which they are destroyed. For particulars of this kind the special books on the subject should be consulted.

Viewed in a broad sense, paint is a liquid material which is applied to the surface of the object to be protected or decorated by means of brushes, or often in these latter days by means of spraying machines.

When so applied and exposed to the air, the paint becomes hard and dry, and forms a protective coating, or it may be perhaps a decorative coating. Paints are of two kinds, according to the character of the liquid medium with which they have been made—First, there are the oil paints, as they are called, in which two liquid media are used, linseed oil and turpentine; and second, there are the distemper or aqueous paints, of which ordinary whitewash is an excellent example, and in which water forms the vehicle or medium. Besides the liquid constituents, paint contains a pigment or a mixture of pigments to which its solidity and colour are due.

The pigments to which, as just stated, paint owes its substance and colour must be bodies which are not subject to chemical alteration when exposed to the weather. In order to possess this feature it is found that they must be insoluble in water. Such substances, for instance, as sugar, sulphate of copper, bichromate of potash, or nitrate of cobalt, all of which are soluble in water, are found to be quite worthless as pigments for painting. Experience has shown that there is nothing better than such natural products as barytes, ochre, umber, Indian red, whiting, china clay, gypsum, or such artificial preparations as white lead, zinc oxide, ultramarine, chrome yellow, &c., for preparing paints from, and these are very largely used for the purpose. It is not, however, every substance insoluble in water that is useful as a pigment; it must also be reducible by grinding to a fine, impalpable, opaque powder, which retains its brilliancy or colour when mixed with oil or with water.

Hæmatite is red, but as it cannot be ground it is not serviceable as a pigment. Sometimes a body acts very satisfactorily when used with water, but not so when used with oil; this is the case with whiting, china clay. Whiting is much used with water in distemper painting, and is most satisfactory for this purpose, remaining perfectly white and opaque; but when mixed with oil, it turns grey and dull.

If one of these pigments be made into a paint simply with water and applied to a wall, the water evaporates away and leaves the pigment on the wall, but in such a loose powdery form that it is easily washed away by the first shower of rain. Under such circumstances its protective powers are but small, while any decorative effect it may have is lost. To counteract this defect it is necessary to combine the pigment with some substance which will make it cohesive as a paint and adhesive to the wall. In the case of aqueous distemper paints, such bodies are found in glue, casein, albumen, &c., which are more

or less soluble in water, and are left behind as a continuous adherent film or coat when the water evaporates, which film by its very slight solubility in water prevents the rain that may fall on the surface from washing the pigment away. By adding substances that lessen the solubility in water the durability of the paint is considerably increased.

Oil paints are composed of pigments, oils (such as linseed), and turpentine. The turpentine imparts to it the right consistency for the easy application of the pigment, while the linseed oil acts as the binding agent and also increases the protective power of the paint.

This is done by the property linseed oil possesses of absorbing oxygen from the air, more especially when spread over a surface in the form of a thin film or coating, and in so doing forming a firm, hard, and tough mass which resists to a considerable extent the vicissitudes of the weather. This property is called "drying," and of all known oils linseed oil possesses it in the highest degree. To this property fuller reference will be made in the chapter on "Paint Oils." The pigment used in oil paint being imbedded in this film or coat of dried oil is caused to adhere to the painted object in a more perfect manner than is possible with aqueous or distemper paints.

In painting the desire is to hide the original surface and to show only the paint. The application of the oil and turpentine, while forming a protective film, will not do this, because the coat of oil that is left is transparent and so the surface is seen through it. It is, therefore, necessary to mix the oil with an opaque substance in order to hide the surface which is being painted, and this is one of the functions of pigments used in paints. It is found that many pigments, like Prussian blue and crimson lake, for example, possess strong colouring powers; but as they are not sufficiently opaque to be employed alone, they must be used with some other pigment which possesses the needful opacity. We find, therefore, that pigments may be divided into two groups—"body" colours and "staining" colours, as they are called. White lead and barytes are very largely used as body colours, for they are very opaque; while chrome yellow, Prussian blue, vermilion, red oxide of iron, chrome green, and crimson lake are examples of staining colours to which the colour of a paint may be due. Some pigments like ochre, umber, red oxide, and Brunswick green possess sufficient opacity to enable them to act both as body and staining colours at the same time.

Water paints dry with a dull surface, while oil paints dry

with more or less lustre which materially enhances the appearance of the paint. It has been found that this lustre, as well as the rapidity with which the paint will dry, is increased by heating, "boiling" it is called, the oil at about 500° F., either with or without the addition of some lead or manganese compounds. Boiled linseed oil is, therefore, one of the essential constituents of a paint.

Varnishes are used, like paints, for the protective effect they have, and also because they increase the decorative effect. They differ from paints in that they do not hide the special characteristics of the surface to which they are applied; this they do because they are transparent, and when applied leave behind a clear lustrous coat, which, if on wood, develops and intensifies any special beauty of grain that wood possesses, as, for instance, bird's-eye maple, walnut, oak, pitch pine, &c.; also they are often applied over painted decorative work on wood in order, first, to increase its beauty by giving it a lustre, and, second, to cause this work to last longer. Varnishes are prepared from various natural resins by preparing solutions of these in various solvents of a volatile character; when the varnish is applied the latter evaporates away, leaving a film of the resin behind. Some resins are notable for their durable character, as, for instance, animi, copal, shellac, &c.; hence the varnish film has considerable resistant power against the destructive action of the weather.

The Paint and Colour Laboratory.—This book is intended to deal with the laboratory methods of preparing pigments, paints, and varnishes, and of testing the materials used in their preparation. Manufacturing processes will not be given in full, but only in outline, although, when a student has worked through all the methods which will be described in the following pages, it will not be difficult in many cases to translate these laboratory methods into manufacturing processes, but for full details of the latter reference should be made to the writer's *Manual of Painters' Colours, Oils, and Varnishes.*

Students of the subject who, by reason of their circumstances, are not able to work in the properly fitted up laboratory of a Technical School or Polytechnic under the guidance of a teacher who can practically demonstrate to them the various methods which will be found described in this book, and show them the use of the apparatus required to carry them out, need not be discouraged from attempting any of them for fear that the necessary apparatus is expensive and beyond their means; such is indeed not the case. They may provide for themselves a

laboratory which may be well within their means, and in which they can carry out not only the experiments herein described, but also others that may from time to time suggest themselves. There is much yet in the paint trade that is obscure and needs some research work to elucidate and make clear, and again a thorough knowledge of the chemistry and properties of pigments and paint materials is not to be gained by simply reading about them in text books, however good these latter may be, but by handling them and experimenting with them under all sorts of conditions and circumstances.

The following hints on what is required in a laboratory may not be without value to the student, who will, however, find it better not to buy everything at once, but to get them as may be required:—

A good firm bench, or work table, should be provided; one about 5 feet long by 2 feet 6 inches wide and 3 feet high will be found very convenient. This ought to be placed in front of a window so that it is well lighted. The space under the table may be used for storing the pieces of apparatus, such as tripod stands, retort stands, filter stands, sand baths, &c., that are made of metal.

If gas is available then the student will provide one or two Bunsen burners or the common small boiling burners. When gas is not available the petroleum oil boiling stoves that can be bought for about 2s. 6d. will be useful in making colours, boiling water, and other similar operations. Spirit lamps are also useful, although the heat they give out is not great. The "Primus" and similar stoves which burn petroleum oil or methylated spirit under pressure will serve to carry on all operations in which a Bunsen burner is required. For some purposes, such as heating crucibles, &c., where a high temperature is required, a plumber's soldering blowpipe burning petroleum oil will be very serviceable.

A balance and weights are very necessary. A good, serviceable chemical balance, quite good enough to carry out all the experiments detailed in the following pages, can be bought for from 25s. to 30s., while, if this is too high a price, a pair of apothecaries' hand scales, costing from 2s. 6d. to 3s. 6d. and used with care, will give good results. A set of gramme weights from 100 grammes to 1 milligramme should be bought. Such will cost 7s. 6d. In using the balance it is a good rule never to put any substance direct upon the pan of the balance, but always to weigh it in a small glass beaker or porcelain basin, taking the tare of this first. By this means any wearing of the pan or

its corrosion by chemical agents is avoided, and the life of the balance thereby prolonged. It is advisable, too, always to use the left-hand pan of the balance for the substance to be weighed and to put the weights on the right-hand pan. When taking the weight of anything always put the balance to rest before taking off or putting on the weights, and put these on in regular order as they occur in the box. Again, as each weight is used put it back in its proper place in the box. These are simple rules, easily carried out, which make for good order, accurate weighing, and preservation of balance and weights. Their non-observance invariably leads to loss of time while weighing, inaccuracy of results, and often loss of weights.

For supporting beakers, basins, &c., over Bunsen burners there will be needed one or two tripod stands; a retort stand fitted with several rings and a clamp will be needed and will serve for a variety of useful purposes, such as holding burettes, as a filter stand, for supporting condensers, &c. A supply of small tin plates, such as can be bought of an ironmonger at a penny each, will be found useful to stand beakers or basins on while being heated over the Bunsen burners.

There will be needed to carry out the experiments described in the following chapters, more especially the quantitative analytical tests, a few glass beakers, funnels, test tubes, porcelain basins, porcelain crucibles, and small flasks.

For making the colours, the small enamelled saucepans which can be bought from most ironmongers at about 6d. each will be found useful. For filtering, ordinary blottingpaper may be used, but for accurate chemical tests filter paper should be provided. For some experiments special apparatus will be required; this may be provided when needed, and will be found described in the proper place. Glass tumblers with thin bottoms, which may be bought for 1d. or 2d., serve admirably for filtering, precipitating, or dissolving with cold or moderately-warm solutions, but they cannot be heated direct over a Bunsen burner.

The student will find it convenient to provide himself with measuring glasses; one cylindrical to hold 100 cubic centimetres, and graduated in c.c., will be useful; flasks graduated to hold 100, 200, and 500 c.c. are very useful; while a few pipettes, 10 c.c., graduated so that 1 or 2 c.c. can be measured, as well as separate 10, 20, and 25 c.c., will often be needed.

In carrying out the experiments on colour making described in the following pages, the student may take larger quantities than are there given, sometimes with advantage, by multiplying

the quantities by 2, 3, or 4; but the operations will be more lengthy; still time is often saved by conducting several experiments concurrently. Such operations as filtering, washing, drying, &c., may take time, but as they do not require constant attention, other experiments may be initiated while waiting for their completion. In fact, a student should cultivate the habit of attending to several sets of experiments, provided there is no risk of their interfering one with another.

This habit is easily acquired when a student has become familiar with the routine of the ordinary manipulations required in carrying out experimental work.

When a beaker has been used for one experiment it must be thoroughly cleaned before using it for another experiment; otherwise the results obtained will be very confusing. In using glass apparatus its fragile nature ought to be kept constantly in mind; glass will stand a considerable amount of heating if the heat is applied gradually, whereas the sudden alteration of heat will crack the glass, especially if it be thick. Cold water dropping on hot glass, or putting a hot glass on a cold surface, will cause the glass to crack.

CHAPTER II.

PREPARATION OF PIGMENT COLOURS.

In the following pages laboratory methods for the preparation of such pigments as the chrome yellows, Brunswick greens, and Prussian blues will be given first, because they can be prepared on a small scale in the laboratory. It is, of course, obvious that the natural colours—barytes, ochre, &c.—cannot well be prepared in the laboratory; still various experiments will be given in connection with these with a view of demonstrating their properties. Methods of testing the pigments so prepared will be described. If the student faithfully follows the directions which will be given he will succeed in his work and obtain a knowledge of the method of making colours, which can be readily applied to working on the large scale. Following this will be given brief outlines of the manufacturing processes and of the composition and properties of the various commercial pigments, but for full details of these the reader is referred to the author's *Manual of Painters' Colours, Oils, and Varnishes.*

In the work just named the various pigments are grouped, according to their colour, into white, red, blue, &c., pigments, but in this book no particular order will be observed. The various pigments will be dealt with more according to ease of preparation, so that the student is carried from stage to stage of difficulty as he gains experience in the manipulation of chemical experiments and chemical apparatus.

CHROME PIGMENTS.

The metal chromium may be said to be the base of some valuable pigments, such as the many grades of chrome yellows and oranges, zinc chrome, Derby red, Guignet's green, &c., and of these the lead compounds are by far the most important.

Chromate of lead, which has the chemical composition shown in the formula $PbCrO_4$, is the base of the yellow, orange, and

red pigments known under the names of chrome yellow, lemon chrome, primrose chrome, American yellow, Cologne yellow, chrome orange, chrome red, Derby red, American vermilion, &c. It may be regarded as a compound of the basic oxide, lead monoxide, or litharge, $Pb O$, and the acid oxide, chromic acid, $Cr O_3$; its preparation will now be described.

PREPARATION OF CHROME YELLOW.—Provide bichromate of potash, or "bichrome," as it is more commonly called, and acetate of lead or white sugar of lead.

Weigh out 5 grammes of the acetate of lead, and dissolve in 100 c.c. of cold water in a beaker. Then weigh out 1·75 grammes of the bichromate of potash and dissolve in 100 c.c. of cold water. In order to facilitate solution it is advisable to powder the salts ; this should be done before weighing. When both are dissolved, pour the bichromate solution into the lead solution, when a bright yellow precipitate of chrome yellow (chromate of lead) will be obtained. Allow the mixture to stand for a few minutes, when it will be found that the yellow will settle down to the bottom, leaving the supernatant liquor clear. Pour this off into a glass beaker. Note that on taking some in a test glass and adding a little litmus solution, a red

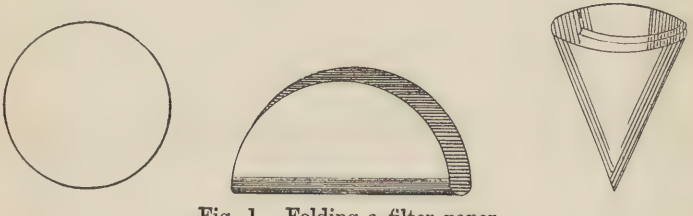


Fig. 1.—Folding a filter paper.

colour is obtained, which shows that it is acid in character, and note further that the liquor smells of acetic acid. This shows that in the reaction which occurs between the bichromate of potash and lead acetate, acetic acid is formed.

Having poured off the top liquor from the precipitate of chrome yellow, add to it a quantity of clean water, stir well, then allow to settle as before and again pour off the clear liquor. While the yellow is settling after this first washing, prepare a filter in which the chrome yellow can be filtered off. A piece of filter paper is taken and folded in half, and again at right angles ; now open one fold, when a cone will be obtained which has one thickness of paper on one half of its surface, and three

thicknesses on the other half. See Fig. 1, which shows stages from the flat paper to the filter cone. The filter is then put into a funnel and wetted with water; the precipitate and the liquor which remains in contact with it are poured in; the liquor runs through, leaving the precipitate on the filter.

Sometimes the filtration proceeds at a very slow rate, owing to the fact that the filter paper clings too closely to the sides of the funnel, while the extra thickness of paper over one-half of the filter impedes the rate of filtering on that section. A better mode of folding the paper, which ensures a great increase in the rate of filtering, is the following:—Fold the paper in half, then open it out and again fold at right angles to the other one; open out the paper and press the paper together between the creases so formed, making a kind of four-rayed star, with the paper meeting in the centre; next flatten the paper, then fold the outer edges to the centre on both sides, open out the paper in the form of a cone (see Fig. 2, which shows the shape of the folded paper), and place in the funnel. Filtration with this method of folding is done in half the time. Fig. 3 shows the filtering apparatus complete, with the funnel, stand, and beaker for the filtered liquid in the best position; while Fig. 4 shows the best method of filtering precipitates, which is by pouring the liquid to be filtered into the funnel down a glass rod, a method to be followed particularly when making a quantitative analysis.

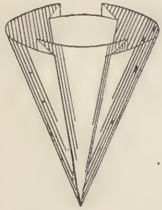


Fig. 2.—Folded filter paper.

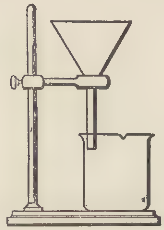


Fig. 3.—Filtering apparatus.

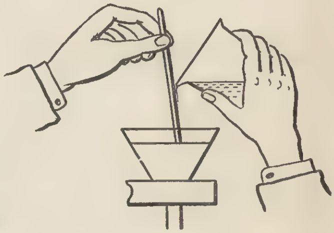


Fig. 4.—Method of pouring.

After all the mass has been poured on the filter, rinse out the beaker with clean water, getting as much as possible of any yellow that may adhere to the side of the beaker, and pouring this on the filter. When all the liquid has gone through, pour some clean water over the colour on the paper, so as to wash it, then dry it by placing the funnel and its contents in a not too hot

oven, or, if that is not handy, place a tin plate on the tripod stand or burner stand; on this place a tin canister with the ends knocked out, and a few holes bored round the edges of the cylinder so formed; into this place the funnel, and a very convenient drying arrangement will be constructed. Fig. 5 shows what is called a "drying cone," and is the form much used in chemical laboratories for drying precipitates. When dried (the slower the better), scrape as much of the yellow as possible off the paper, and weigh it so as to ascertain the yield of colour obtained from the materials used.

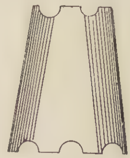


Fig. 5.--Drying cone.

The reaction which takes place between the potassium bichromate and lead acetate is one of double decomposition. The potassium bichromate is a compound of chromic acid and potassium, the lead acetate one of acetic acid and lead; the latter leaves the acetic acid, and combines with the chromic acid to form the chromate of lead. This it does because the latter is an insoluble body, and it is one of the principles of double decomposition that when two soluble compounds in the form of solution are mixed together, and these bodies contain constituents that if combined together form an insoluble substance, then this latter falls out of the solution in the form of a precipitate.

We may represent the reaction which takes place between the bodies in the form of a chemical equation, thus—

$$\underset{\text{Potassium bichromate.}}{K_2Cr_2O_7} + \underset{\text{Lead acetate.}}{2Pb\,2C_2H_3O_2} + \underset{\text{Water.}}{H_2O} = \underset{\text{Lead chromate.}}{2PbCrO_4} + \underset{\text{Potassium acetate.}}{2KC_2H_3O_2} + \underset{\text{Acetic acid.}}{2HC_2H_3O_2}.$$

From this equation we see that three substances enter into the reaction—potassium bichromate, lead acetate, and water, the formula for which are put on the left-hand side of the = sign (which in connection with chemical equations should not read as meaning exactly "equals," but rather in the sense of "forms"); while there are three substances formed—lead chromate, potassium acetate, and acetic acid—the formula for which are placed on the right-hand side of the = sign.

From this equation we can calculate how much of the reacting compounds take part in the reaction and how much of the substances formed are produced, for chemical formulæ always stand for known weights of the substances they represent. Thus in the case in question, the formula $K_2Cr_2O_7$ stands for 295 parts by weight of potassium bichromate, $Pb\,2C_2H_3O_2$ for 325 parts

by weight of lead acetate, and twice this quantity, or 650 parts, are required for the 295 parts of bichromate of potash.

Similarly, H_2O stands for 18 parts by weight of water, $PbCrO_4$ represents 323·5 parts of lead chromate, $KC_2H_3O_2$ stands for 98 parts of potassium acetate, and $HC_2H_3O_2$ for 60 parts of acetic acid. The equation shows, then, that 295 parts of potassium bichromate react with 650 parts of lead acetate and 18 parts of water to form 647 parts of lead chromate, 196 parts of potassium acetate, and 120 parts of acetic acid.

These proportions are those which are theoretically required to carry out the operation or are produced thereby. If more of the lead acetate, for instance, were used, then whatever is in excess does not take part in the reaction, but remains unchanged and is wasted. A chemical equation is therefore valuable in that it shows in which proportions ingredients can be mixed together to bring about chemical reactions without waste.

In place of using lead acetate, lead nitrate is frequently used in the manufacture of chrome yellows; the process is precisely the same. In this case the reaction is shown by the equation—

$$\underset{\text{Potassium bichromate.}}{K_2Cr_2O_7} + \underset{\text{Lead nitrate.}}{2Pb2NO_3} + \underset{\text{Water.}}{H_2O} = \underset{\text{Lead chromate.}}{2PbCrO_4} + \underset{\text{Potassium nitrate.}}{2KNO_3} + \underset{\text{Nitric acid.}}{2HNO_3}.$$

295 parts of potassium bichromate require 662 parts of lead nitrate and 18 parts of water to produce 647 parts of lead chromate, 202 parts of potassium nitrate, and 126 parts of nitric acid.

The tint or shade of chrome yellow obtained is much modified by the conditions under which it is precipitated, such as strength of solutions, temperature, &c. It will be worth the while of the student to test the effect of temperature, and this he may very easily do by following the above instructions, but using hot water to dissolve the salts, and precipitating while still hot. After drying, compare the tints of the two samples of yellows made with cold solutions and with hot solutions; while by using less water, the effect of varying strength of solution can be seen.

After having made the yellow it is as well to make a few tests with it. This can be done by placing a little of the yellow in test tubes, and adding various reagents as follows :—

1. Boil with a little strong hydrochloric acid. Note that the yellow is completely dissolved, that the solution becomes green, a characteristic feature of chromates, and that on cooling, white crystals of lead chloride, $PbCl_2$, fall down, a characteristic reaction of lead.

2. Heat with a little strong sulphuric acid for a short time, then allow to cool, and add some water. Note that the solution is green, and that a white precipitate of lead sulphate, $Pb\,S\,O_4$, is left behind.

The change of colour from yellow or orange or red to green by the action of acids is eminently characteristic of all chrome colours. The formation of crystals of lead chloride with hydrochloric acid and of lead sulphate with sulphuric acid, as seen in experiments 1 and 2, is very characteristic of lead.

3. Boil with a strong solution of caustic soda. Note that the colour of the yellow first becomes orange, then red, and, lastly, that it dissolves.

In making qualitative tests like these, it is a good rule to take only small quantities of the substance to be tested.

Having made the above qualitative tests, the student will be in a position to make a quantitative analysis of the chrome yellow.

The chrome yellow, made as previously described, will consist of lead chromate only, and to make a quantitative analysis of it, two constituents, the lead and the chrome acid, only have to be determined; accordingly, a quantitative analysis of lead chromate is made in the following manner. The sample to be analysed should be carefully dried at a gentle heat so as to ensure its freedom from water.

Place the dried and powdered sample in a small stoppered weighing bottle, which is now put on the left-hand pan of the chemical balance and carefully weighed, noting the weight.

Provide a clean beaker, shake some of the yellow from the weighing bottle into the beaker, and weigh the bottle again. The difference between the weights obtained in the two weighings is the weight of the chrome yellow taken; this quantity should not exceed 1 gramme.

Now pour over the yellow about 15 c.c. of pure, strong sulphuric acid, and heat on a sand bath over the Bunsen burner until the yellow appears to be thoroughly decomposed, a white powder (lead sulphate) and a green solution being obtained.

Allow the mass to get cold and dilute with plenty of water, and add a little alcohol; filter carefully, taking care to get all the white precipitate or residue on to the filter. This can be done by washing the precipitate from the sides of the beaker by means of a wash bottle, such as is shown in Fig. 6, perhaps assisted by means of a brush made by slipping a little bit of rubber over the end of a glass rod. It is important in order to ensure accuracy of results that all the precipitate should be

got on the filter paper. Wash well with clean warm water. Now place the filter and its contents in the drying cone shown in Fig. 5, and dry it. While this is being done, clean out a porcelain crucible and dry it over a Bunsen burner, allow it to get quite cold in a desiccator, then weigh it.

Place the crucible on a sheet of clean black glazed paper, transfer as much of the precipitate of lead from the filter into the crucible as possible, next place the top of the crucible on a triangle made from bits of tobacco pipes over the Bunsen burner and put the filter paper on it. All the paper will burn away, and when it is completely burnt away and a white ash is left, allow to cool, add a single drop of strong nitric acid, followed by a drop of strong sulphuric acid; then heat until all acid fumes cease to come off; allow the lid and its contents to cool, transfer them to the main bulk of the lead sulphate in the crucible, heat all over the Bunsen burner for about twenty minutes, then allow to cool, and weigh; the weight of the lead sulphate formed will thus be obtained.

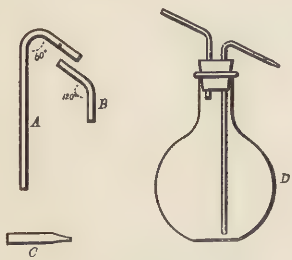


Fig. 6.—Wash bottle.

From the weight of lead sulphate obtained the weight of the lead oxide it contains may be calculated in the way shown by the following example:—

Weight of Lead Chromate taken.

Weight of bottle and yellow, 1st, .	12·432
,, bottle, 2nd, . . .	11·219
Weight of yellow taken, . .	1·213
Weight of crucible and lead sulphate,	9·435
,, crucible, ...	8·324
,, lead sulphate and filter ash,	1·111
,, filter ash, ...	·002
,, lead sulphate, . . .	1·109

As $PbSO_4 = PbO$ indicates that 303 parts of lead sulphate contain 223 parts of lead oxide, the proportion sum

$$303 : 223 :: 1{\cdot}109$$

shows that the lead sulphate obtained contains 0·816 of lead oxide, while the proportion sum

$$1{\cdot}213 : 0{\cdot}816 :: 100$$

shows that the sample of chrome yellow taken contains 67·27 per cent. of lead oxide.

The chromic acid will be found in the filtrate; boil this down a little, and when sufficiently concentrated add a slight excess of ammonia; a violet or green precipitate of chromium hydroxide, $Cr_2 H_6 O_6$, is thrown down. This is filtered off. The filtrate ought to be colourless; if it has a pinkish tint it indicates that some of the chromium has been kept in solution by the ammonia; in this case boil well, when the dissolved chromium will be precipitated. Filter this. Well wash, dry, and transfer the precipitate to a weighed porcelain crucible; keep this at a bright red heat for some time, then allow to cool and weigh. The residue in the crucible is chromic oxide, $Cr_2 O_3$, and from its weight the proportions of the chromic acid in the lead chromate may be calculated according to the factor $Cr_2 O_3 = 2 Cr O_3$; 153 parts of chromic oxide = 201 parts chromic acid.

The following will be the weights obtained:—

Weight of crucible and chromium oxide,	8·619
,, crucible,	8·324
	·295
,, filter ash,	·002
,, chromium oxide,	·293

The proportion sum

153 : 201 : : 0·293,

shows that the same contained 0·385 gramme of chromic acid, or

1·213 : 0·385 : : 100,

31·73 per cent. of chromic acid.

Summing up the results we have the sample of chrome yellow containing—

66·27 per cent. of lead oxide, Pb O.
31·73 per cent. of chromic acid.

98·00

PREPARATION OF LEAD SULPHATE.—Weigh out 5 grammes of lead acetate and dissolve in 100 c.c. of water; then weigh out 5 grammes of Glauber's salt (crystallised sodium sulphate) and dissolve in 100 c.c. of water. When both solutions are ready add the sodium sulphate to the lead solution when a white precipitate of sulphate of lead, $Pb S O_4$, will be obtained; this should be collected and weighed in the same manner as was done with the chrome yellow.

The reaction which occurs between the two salts is shown in the following equation :—

$$Na_2SO_4 + Pb2C_2H_3O_2 = PbSO_4 + \underset{\text{Sodium acetate.}}{2NaC_2H_3O_2}.$$

Instead of using sodium sulphate, Na_2SO_4, to precipitate the lead salt, sulphuric acid, H_2SO_4, may be employed; in this case the reaction is—

$$H_2SO_4 + Pb2C_2H_3O_2 = PbSO_4 + \underset{\text{Acetic acid.}}{2HC_2H_3O_2},$$

from which it will be seen that free acetic acid is obtained; when, for certain purposes, lead sulphate pure and simple is required this is the most convenient way of preparing it, as the acetic acid so set free may be used to dissolve granulated lead or litharge to make a new solution of lead from which to precipitate the lead sulphate.

Having prepared the lead sulphate, its properties may be investigated by the following experiments carried out in the test tubes :—

1. Warm it with dilute nitric acid, when it will be found to be insoluble.

2. Boil with strong hydrochloric acid, when it will dissolve slowly. On allowing the solution to cool, transparent crystals of lead chloride will fall down.

3. Boil with a solution of caustic soda, when it will dissolve.

LEMON CHROME, PRIMROSE CHROME.

Under the above names, and also such as pale chrome, American yellow, Cologne yellow, &c., are sold chrome pigments of a greenish-yellow tint, varying somewhat in depth of shade. These consist of a mixture, in varying proportions, of chromate of lead and sulphate of lead. It is, of course, obvious that by adding the white sulphate of lead to the deep yellow chromate of lead, the colour of the mixture will be paler than the colour of the latter compound, and will be paler in proportion to the quantity of lead sulphate the mixture contains.

PREPARATION OF LEMON CHROME.—Weigh out 5 grammes of lead acetate, and dissolve in 100 c.c. of water. Also weigh out 1·25 grammes of Glauber's salt (crystallised sodium sulphate) and 1·25 grammes potassium bichromate, and dissolve the two salts together in 100 c.c. of water. Both solutions must be cold. When ready, pour that of the bi-

chromate and sulphate into the lead solution, when the lemon chrome will be precipitated; filter off the precipitate, wash it with water, dry it, and weigh it.

Tests for the Yellow.—1. Boil with strong hydrochloric acid. Note the change of colour to green. Divide the solution into two parts; allow one to cool, and note the crystals of lead chloride which fall down; to the other portion add a solution of barium chloride; note the white precipitate of barium sulphate, insoluble on boiling, which is obtained. Chrome yellow does not give this latter reaction.

2. Treat the yellow with water and a little nitric acid, and warm gently. Note that a yellow solution and a white residue are left behind, this latter being the lead sulphate.

3. Boil with caustic soda, and note that it is entirely soluble.

Lemon chrome, as thus prepared, is a mixture of lead chromate, $Pb\,Cr\,O_4$, and lead sulphate, $Pb\,S\,O_4$, and its formation is represented by the equation—

$$3\,Pb(C_2H_3O_2)_2 + K_2Cr_2O_7 + Na_2SO_4 + 2\,H_2O =$$
$$2\,PbCrO_4PbSO_4 + 2\,KC_2H_3O_2 + 2\,NaC_2H_3O_2 + 2\,HC_2H_3O_2.$$

The proportion of $Pb\,Cr\,O_4$ to $Pb\,S\,O_4$ in the lemon chrome will depend upon the proportions of potassium bichromate and sodium sulphate used; the more there is of the former to the latter the more lead chromate there will be in the pigment which is made, and the deeper the tint of the resulting product. In making these lemon yellows, if the proportion of bichromate be increased that of the sulphate should be decreased, and *vice versâ;* the two salts stand in the following ratios to one another:—1 lb. of bichromate of potash is equal to 2·5 lbs. of Glauber's salt; 1 lb. of Glauber's salt is equal to 0·4 lb. of potassium bichromate.

The student would do well to make several lots of lemon yellow, varying the proportions of bichromate of potash and Glauber's salt as indicated above.

In place of using Glauber's salt sulphuric acid may be used, 98 parts of which are equal to 322 parts of Glauber's salt in precipitating power. Care must be taken not to use an excess of sulphuric acid, or else such excess may prevent any precipitation of chrome yellow.

PREPARATION OF CHROME RED.—Weigh out 5 grammes of lead acetate and 1·75 grammes of potassium bichromate; dissolve each separately in 100 c.c. of water; then mix the two solutions, allow the precipitate of chrome yellow to settle out, pour off the supernatant liquor, add a

solution of 0·75 gramme of caustic soda in 50 c.c. of water and boil for about half an hour, or until the yellow has assumed a red colour; then filter, wash, and dry. The red so produced will answer to the same tests as the chrome yellow first described.

The student will understand the chemical reactions so far as the formation of the chrome yellow is concerned. That for its transformation into chrome red depends upon the fact that caustic soda is a stronger base than lead, and when the chrome yellow is boiled with the alkaline solution, it is partially decomposed; the caustic soda takes chromic acid from the chromate of lead forming chromate of soda (which is soluble) and passes into the liquors; hence these have a yellow colour; while the oxide of lead, liberated at the same time, enters into combination with the residual chromate of lead to form a basic chromate, which is red. This reaction is expressed in the equation—

$$2\,PbCrO_4 + 2\,NaOH = \underbrace{PbCrO_4PbO}_{\text{Basic lead chromate.}} + \underbrace{Na_2CrO_4}_{\text{Sodium chromate.}} + H_2O.$$

This red pigment is sold under the names of Derby red, Chinese red, Persian red, American vermilion, &c. It is not usual to prepare it in the manner above indicated, but from a mixture of white lead, potassium bichromate, and caustic soda. Several methods are followed; one available for use in the laboratory is detailed below.

PREPARATION OF DERBY RED.—Weigh out 10 grammes of white lead; mix with a solution of 3 grammes of potassium bichromate dissolved in water, to which just enough caustic soda has been added as will change the colour of the solution from orange to yellow; then heat to the boil and keep at that heat till the full red colour is obtained; then wash with water (it is best to use a little sulphuric acid in the last wash water—4 in 400), then dry.

Chrome red, however made, answers to the same tests as chrome yellow.

PREPARATION OF CHROME ORANGE.—Weigh out 5 grammes of lead acetate, and dissolve in 100 c.c. of water. Next weigh out 1·25 grammes of potassium bichromate and 1·25 grammes of Glauber's salt, dissolving them in 100 c.c. of water. Mix the two solutions together, allow the precipitate to settle, pour off the clear liquor, then add a solution of ½ gramme of caustic soda in 100 c.c. of water, heat the mixture for about twenty minutes at the boil, then filter, wash well, and dry.

This new product answers the same tests as the lemon chrome, but differs in colour, being an orange.

The formation of this orange is explained by the conversion of part of the chrome yellow into the basic chrome red (see above), and this, mixing with the unchanged yellow, produces the orange tint; for red and yellow pigments when mixed together produce orange. By using a larger quantity of caustic soda than that given above, a redder shade of orange chrome is obtained, for, in this case, a larger proportion of the chrome yellow is altered to the red; so that the colour maker can, by using more or less alkali, produce orange chromes of varying shade from a yellowish-orange to a scarlet-orange. The student can try experiments based on this principle.

The tests for these orange chromes are the same as for the lemon chrome given above.

The student would do well to make a quantitative analysis of each of the colours described above, by the methods detailed under the head of "Chrome Yellow." The total lead, by heating with sulphuric acid; the chromium, by precipitation with ammonia; and the sulphate, by solution in hydrochloric acid and precipitation with barium chloride.

To do this, weigh out about 2 grammes of the orange chrome, boil with strong hydrochloric acid, and, when dissolved and still boiling, add a solution of barium chloride; a white precipitate of barium sulphate ($Ba\,S\,O_4$) is obtained; this is filtered off and well washed with boiling water, so as to ensure complete removal of all traces of lead chloride; after the washing the barium sulphate is dried, burnt in a crucible, and weighed; from its weight, that of the sulphuric acid anhydride ($S\,O_3$) in the sample may be calculated from the proportion—

$$\underset{233}{Ba\,S\,O_4} = \underset{80.}{S\,O_3}$$

Or the corresponding weight of $Pb\,S\,O_4$ from the proportion—

$$\underset{233}{Ba\,S\,O_4} = \underset{303,}{Pb\,S\,O_4}$$

that is, 233 parts of barium sulphate are equal to 303 parts of lead sulphate.

The amount of moisture should not be neglected or the results will not add up to 100. In calculating the composition from the figures obtained in the analytical operations, the chromium should be reckoned to lead chromate by multiplying the weight of the precipitate of chromium oxide obtained by 4·23; then the amount of lead oxide corresponding to this is calculated by

multiplying the same weight by 2·9. The amount of barium sluphate obtained multiplied by 1·3 gives the amount of lead sulphate, while if it be multiplied by 0·927 it gives the amount of lead oxide present as sulphate. The amount of lead oxide present as chromate or as sulphate, deducted from the total lead oxide found, gives the amount of oxide which is present in the chrome in the free condition.

PREPARATION OF LEMON CHROME.—Weigh out 10 grammes of white lead; mix with 200 c.c. of water and 2 grammes of nitric acid; stir well until all effervescence has ceased; then add 2 grammes of potassium bichromate dissolved in 50 c.c. of water; allow to settle, decant, filter, wash, and dry as described above.

In this case the nitric acid acts upon and dissolves part of the white lead, forming nitrate of lead which is soluble in the water; on adding the potassium bichromate the two salts react with one another; lead chromate is precipitated, and this becomes mixed with the undissolved white lead to form the lemon chrome.

By keeping the nitric acid and potassium bichromate fixed quantities, about equal weights of each and varying the quantity of white lead, varying shades of chrome yellow from deep to pale are obtained.

PREPARATION OF MEDIUM CHROME YELLOW.—Weigh out 5 grammes of lead acetate; dissolve in 200 c.c. of water; mix with this solution 10 grammes of barytes, then add a solution of $1\frac{1}{2}$ grammes of potassium bichromate in 50 c.c. of water. Proceed in the same manner as described above.

In this case the white colour of the barytes tones down the deep yellow of the lead chromate, and so a pale chrome is got. By adding more or less of the barytes varying shades can be obtained. If the precipitated yellow be boiled with caustic soda, or lime, orange chromes are obtained. By using barytes in the manner shown here cheaper grades of chrome yellows (or oranges) are got than is possible to make with any of the other processes. Those chrome yellows, &c., which are not made with barytes are commonly denominated "pure" chrome colours as a distinguishing mark from the grades which are frequently made with barytes, gypsum, and similar white pigments.

The student will have learnt from the above the chemical principles which underlie the preparation of the chrome colours and also something of the processes of manufacture.

MANUFACTURE OF CHROME COLOURS ON THE LARGE SCALE.

Chrome yellows, oranges, and scarlets are made in large wooden tubs, three of which are usually arranged in a set. One, a large one, is placed on the floor, while the other two are somewhat smaller and placed on a staging above the large tub. These latter serve for dissolving the lead acetate, potassium bichromate, and Glauber's salt; always keep the same vat for the same salt; it does not do to dissolve first one and then the other in a vat.

In the bottom vat may be mixed any barytes, gypsum, white lead, &c., that is to be used in the preparation of the pigment. These vats may be supplied with leaden steam pipes for the purpose of heating the various liquors if necessary, and pipes and taps for the supply of water should be fixed above them.

When the solutions are ready the "striking" of the colour is proceeded with in the following manner:—The lead solution is run down in the bottom vat, then any Glauber's salt (if that is used), and, lastly, the bichromate of potash, stirring well all the time. When all has been run in, the colour is allowed to settle out, then the clear top liquor is run off and fresh water run in to wash the colour free from the acetate of soda or nitrate of soda that is formed; for if these are left in their tendency is to make the colour gritty in feel. Stir the colour well with the wash water and again allow to settle, and then run off the clear top water. In making fine colours this washing may be repeated with advantage to the quality of the pigment. After running off the top liquor the colour is passed through the filters and then dried.

The subject of filtering and drying of pigment colours is fully discussed in the author's *Manual* to which reference can be made.

The formulæ which follow will give some idea of the proportions and quantities of materials for preparing various lead chrome colours on a large scale.

Pure Lemon Chrome.—1. Lead acetate or nitrate, 2 cwts.; bichromate of potash, 56 lbs.; Glauber's salt, 76 lbs.

2. Lead acetate, 2 cwts.; bichromate of potash, 40 lbs.; sulphuric acid, 42 lbs.

3. White lead, 300 lbs.; nitric acid, 40 lbs.; potassium bichromate, 35 lbs.

Pure Medium Chrome Yellow.—1. Lead acetate, 2 cwts.; bichromate of potash, 67 lbs.; Glauber's salt, 47 lbs.

2. Lead acetate, 2 cwts.; bichromate, 40 lbs.; sulphuric acid, 27 lbs.

3. White lead, 200 lbs.; nitric acid, 40 lbs.; bichromate, 35 lbs.

Pure Deep Chrome Yellow.—1. Lead acetate, 2 cwts.; bichromate, 78 lbs.

2. Lead acetate, 2 cwts.; bichromate, 56 lbs.; sulphuric acid, 18 lbs.

The chromes made with sulphuric acid, as in the above formulæ, are often called Cologne yellows.

American Chrome Yellow.—Deep—Lead acetate, 2 cwts.; bichromate, 45 lbs.; alum, 2 cwts.; barytes, 90 lbs. Medium—Lead acetate, 2 cwts.; bichromate, 45 lbs.; alum, 2 cwts.; barytes, 1 cwt. Pale—Lead acetate, 2 cwts.; bichromate, 45 lbs.; alum, 2 cwts.; barytes, 1 cwt.; gypsum, 1 cwt.

Lemon Chrome.—Lead acetate, 2 cwts.; barytes, 8 cwts.; bichromate, 77 lbs.

Medium Chrome.—Lead acetate, 2 cwts.; barytes, 4 cwts.; bichromate, 77 lbs.

Deep Chrome Orange.—1. Lead acetate, 77 lbs.; bichromate, 20 lbs.; caustic soda, 5 lbs.

2. Lead acetate, 2 cwts.; bichromate, 65 lbs.; Glauber's salt, 45 lbs.; quicklime, 23 lbs.

3. Lead acetate, 2 cwts.; barytes, 1½ cwt.; bichromate, 77 lbs.; quicklime, 23 lbs. By using more Glauber's salt or barytes paler oranges are made.

Scarlet Chrome.—1. Lead acetate, 2 cwts.; bichromate, 77 lbs.; caustic soda, 28 lbs.

2. White lead, 2 cwts.; bichromate, 67 lbs.; caustic soda, 28 lbs.

Chrome Red, Derby Red.—1. White lead, 2 cwts; bichromate, 1 cwt.; caustic soda, 35 lbs.

2. White lead, 2 cwts.; bichromate, 68 lbs.; mix with 150 gallons of water and 18 lbs. of caustic soda; allow to stand for two days, stirring at intervals, then boil for half an hour to fully develop the reds; wash twice with water; if the last wash waters contain a little sulphuric acid the fire of the red is increased.

PROPERTIES OF THE LEAD CHROMES.—From the tests described under each of the various varieties of the lead chromes, the chemical properties of this pigment will be gathered. The following remarks concerning their properties as pigments are taken from the author's *Manual*, p. 134, third edition:—

The lead chromes are pigments of considerable brilliance of hue, and their covering power or body is very great, being superior to that of all other yellow colours, so that it is very difficult to find substitutes for them. The texture of these pigments is usually very fine, but there is considerable difference between the products of different makers in this respect. When well made they are very durable colours, exposure to all the ordinary atmospheric influences—heat, light, air, and moisture—having very little injurious action on them. Sulphuretted hydrogen and sulphur compounds turn them black, owing to the formation of the black sulphide of lead; some samples show a tendency to acquire a green hue when mixed with oil, which is due to an action between the chromic acid of the colour and the oil; probably in most cases when this occurs, the action has been set up, in the first instance, by a small quantity of alkaline chromate left in the colour owing to defective washing, and this, having a powerful action upon the oil, oxidises it, and, at the same time, turns it green; this action having once been set up gradually extends throughout the mass of colour affected. This defect is more likely to happen with the oranges, scarlets, and reds than with the yellows.

The chromes are capable of being mixed with a large number of other pigments without being themselves affected or affecting others. It is not advisable to mix the chromes with pigments like ultramarine and cadmium yellow, which contain sulphur, as the mixture is apt to take a reddish tone, owing to the formation of a black sulphide of lead. Highly basic colours should not be mixed with chromes, as then they turn orange. Chrome yellows do not work well with whiting in distemper work, as they sometimes turn orange, but the oranges and reds may be so used.

Chrome yellow cannot be used along with lime or silicate of soda, or other alkaline vehicle, as these will turn them orange. This red seems to have a crystalline nature, which it will lose by friction; in doing so it turns of an orange colour; care must, therefore, be taken not to grind the red too much.

The following analyses of various chrome pigments will give some idea of their average composition :—

Pure Primrose Chrome.

Water,	7·43	per cent.
Lead chromate,	55·24	,,
Lead sulphate,	37·33	,,

Primrose Chrome.

Water,	6·84	per cent.
Lead chromate,	58·12	,,
Barytes,	35·04	,,

Pure Pale Chrome.

Water,	2·16	per cent.
Lead chromate,	56·14	,,
Lead sulphate,	30·14	,,
Lead oxide,	11·46	,,

Pale Chrome.

Water,	5·28	per cent.
Lead chromate,	57·12	,,
Barytes,	37·60	,,

Pure Middle Chrome.

Water,	2·16	per cent.
Lead chromate,	86·54	,,
Lead sulphate,	8·34	,,
Lead oxide,	2·96	,,

Middle Chrome.

Water,	5·32	per cent.
Lead chromate,	80·54	,,
Barytes,	4·32	,,
Gypsum,	9·82	,,

Pure Deep Chrome.

Water,	5·46	per cent.
Lead chromate,	72·14	,,
Lead sulphate,	10·54	,,
Lead oxide,	11·86	,,

Deep Chrome.

Water,	3·34	per cent.
Lead chromate,	75·16	,,
Lead oxide,	9·45	,,
Barytes,	12·05	,,

Pure Orange Chrome.

Water,	3·14	per cent.
Lead chromate,	61·52	,,
Lead oxide,	25·34	,,

Pure Scarlet Chrome.

Water,	2·85	per cent.
Lead chromate,	60·83	,,
Lead oxide,	36·32	,,

Derby Red.

Water,	2·12	per cent.
Lead chromate,	57·42	,,
Lead oxide,	40·46	,,

ZINC CHROME.

Zinc chrome is the chromate of the metal zinc, and has a composition corresponding to the formula $Zn\,Cr\,O_4$.

PREPARATION OF ZINC CHROME.—Weigh out 8·2 grammes of crystallised sulphate of zinc, and dissolve in 100 c.c. of water; heat gently, and now add to the solution, drop by drop, a solution of sodium carbonate, stirring well all the time. The first few drops may produce no effect, but presently a white precipitate will form. When this happens the addition of the sodium carbonate is stopped. The object is to prepare a perfectly neutral solution of the zinc sulphate.

Next weigh out 5 grammes of potassium bichromate and dissolve in 50 c.c. of water. This solution must be neutralised, for potassium bichromate, being acid in character, will not precipitate zinc salts. The neutralisation is best affected by warming the solution and adding a solution of caustic soda, drop by drop, until a drop of the mixture, taken out and dropped upon a piece of paper moistened with phenolphthalein solution, forms a red spot. The two solutions are then mixed, when a yellow precipitate of the zinc chrome will be obtained. This can be filtered off, washed with water, dried, and weighed.

Provided the instructions given above are carefully carried out a good yellow will be obtained, but if the solutions used have not been properly neutralised and are acid, no precipitate will form, while, if the solutions be made too alkaline, then a white gelatinous precipitate of zinc hydroxide will be obtained. The zinc chrome comes down as a fine, pale yellow, amorphous precipitate.

The reaction which takes place is expressed in the following equation—

$$\underset{\text{Potassium chromate.}}{K_2CrO_4} + \underset{\text{Zinc sulphate.}}{ZnSO_4} = \underset{\text{Zinc chromate.}}{ZnCrO_4} + \underset{\text{Potassium sulphate.}}{K_2SO_4}.$$

Test the zinc chrome, thus made, as follows :—

1. Treat with dilute sulphuric acid; it completely dissolves to a yellow solution. Here one point of distinction from chrome yellow will be noticed. It is also soluble in dilute hydrochloric acid.

2. Heat with strong hydrochloric acid; a green solution will be obtained. This change of colour from yellow to green is quite characteristic of chromates, as already pointed out in connection with the lead chromes.

If to this green hydrochloric acid solution ammonia be added, a greenish precipitate of chromium hydroxide will be obtained. If this be filtered off and ammonium sulphide be added to the filtrate, a white precipitate of zinc sulphide will be obtained.

The purity of a sample of zinc chrome can be ascertained by the results of these tests.

A quantitative analysis of zinc chrome is made as follows :—2 grammes of the sample should be weighed out and dissolved by boiling with strong hydrochloric acid and a little alcohol; this latter is added to ensure that all the chromium shall be converted into the basic chromium chloride. Now add ammonia in but slight excess, boil well, filter off the precipitate of chromium hydroxide, wash it with clean water, adding the first washings to the filtrate, which must be kept. The precipitate is dried, burnt in a crucible, and the residue of chromium oxide, Cr_2O_3, weighed. The weight of this multiplied by 3·322 gives the weight of actual zinc chromate in the sample.

To ascertain the amount of the zinc, take the filtrate from the chromium precipitate, heat to the boil, and add to it ammonium sulphide in slight excess. This throws down the zinc as sulphide, ZnS; filter off, wash well with warm water, dry, and burn over the Bunsen in a crucible. This must be well done in a good current of air, otherwise the zinc sulphide will not be fully converted into zinc oxide, as it ought to be. The weight of zinc oxide, ZnO, which is obtained, multiplied by 2·239, gives the weight of the zinc chromate in the sample. This should be the same as that calculated from the chromium precipitate.

PREPARATION OF ZINC CHROME.—Another method of making this pigment is to heat together zinc oxide, potassium bichromate, and water. Weigh out in a beaker 8 grammes of zinc oxide (zinc white) and 7·5 grammes of potassium bichromate; add 100 c.c. of water, and boil together for half an hour; then filter, wash, and dry, and weigh the zinc chrome that is formed. The filtrate from the chrome has a yellow colour, showing that it contains potassium chromate in solution.

The reaction which takes place is shown in the following equation :—

$$\underset{\text{Zinc oxide.}}{ZnO} + \underset{\text{Potassium bichromate.}}{K_2Cr_2O_7} = \underset{\text{Zinc chromate.}}{ZnCrO_4} + \underset{\text{Potassium chromate.}}{K_2CrO_4}$$

The zinc oxide, combining with the excess of chromic acid in the bichromate forms zinc chromate and normal potassium chromate.

The chrome yellow thus made can be examined by the tests described above.

MANUFACTURE OF ZINC CHROME.—This pigment is made in the same kind of vats as described under chrome yellow. There can be used in its manufacture 145 lbs. of crystallised zinc sulphate and 76 lbs. of potassium bichromate; both are neutralised by the addition of sodium carbonate, as in the laboratory method, taking care to avoid excess of alkali. As little liquor as possible is used, and this hot. It is also made by boiling zinc oxide and bichromate together, a process originally patented by James Murdock in 1847, who gives formulæ for producing various shades of zinc chrome by its means. This is not a very good method.

COMPOSITION AND PROPERTIES.—Zinc chrome is essentially the chromate of zinc, having the formula $ZnCrO_4$, and consisting of—

Zinc, Zn, ...	35·81 per cent.
Chromium, Cr, ...	28·93 ,,
Oxygen, O, ...	35·26 ,,

or,

Zinc oxide, ZnO, ...	44·63 per cent.
Chromic acid, CrO_3, . . .	55·37 ,,

The composition of the commercial article is fairly pure, containing perhaps a little water and oxide of zinc, as shown in the following analysis made by the author:—

Water, ...	16·08 per cent.
Zinc chromate, ...	38·99 ,,
Zinc oxide, ...	44·93 ,,

It is a pigment of good colour and body, quite permanent, resisting exposure to light and air when well made; sulphurous gases have no effect on it. It can be mixed with all other colours without being changed by them or changing them in any way.

When pure, zinc chrome is soluble in acetic or nitric acids without effervescence, any yellow residue would indicate adulteration with lead chrome or yellow ochre. A white residue would indicate adulteration with barytes or gypsum. Effervescence with acids would indicate adulteration with whiting or white lead. Pure zinc chrome is not altered on the addition of ammonium sulphide. Caustic soda and ammonia dissolve zinc chrome when in excess.

BARIUM CHROME.

Barium chrome is the chromate of the metal barium, having the formula $Ba\,Cr\,O_4$.

PREPARATION OF BARIUM CHROME.—Weigh out 7·5 grammes of potassium bichromate and 5·6 grammes of barium chloride; dissolve each separately in 100 c.c. of water; then mix the two solutions, filter off the precipitate of barium chromate which is formed, wash, and dry as described under chrome yellow.

It is best to neutralise the bichromate solution with caustic soda as described under zinc chrome.

Examine it by the following tests:—

Treat with a little dilute hydrochloric acid, when it will completely dissolve.

Heat with sulphuric acid, when a white precipitate of barium sulphate and a green solution of chromium sulphate will be obtained.

These two tests will, by their results, distinguish barium chrome from either lead chrome or zinc chrome. Barium chrome consists of barium chromate, $Ba\,Cr\,O_4$, and its formation is shown in the following equation:—

$$\underset{\text{Potassium chromate.}}{K_2\,Cr\,O_4} + \underset{\text{Barium chloride.}}{Ba\,Cl_2} = \underset{\text{Barium chromate.}}{Ba\,Cr\,O_4} + \underset{\text{Potassium chloride.}}{2\,K\,Cl.}$$

As a pigment it is of little value, being deficient in depth of colour and in opacity, the two chief properties which are required in pigments.

PRUSSIAN BLUE.

One of the most important of the blue pigments is that known as Prussian blue, Chinese blue, Berlin blue, Paris blue, &c. This was discovered accidentally about 1704 by a Berlin colour maker named Diesbach, and from this circumstance received the names of Prussian blue and Berlin blue. It will be convenient to consider this pigment next, and to make it by several methods, and then to speak more fully of its chemical composition and properties.

PREPARATION OF PRUSSIAN BLUE.—Weigh out 5 grammes of the yellow prussiate of potash (potassium ferrocyanide) and 5 grammes of green copperas (ferrous sulphate);

dissolve each in 100 c.c. of water; add a few drops of hydrochloric acid to each, and then mix the two solutions, when a pale blue or white precipitate of ferrous or iron ferrocyanide will fall down. Now slowly add to the mixture 2 grammes of bleaching powder, when the white precipitate will be changed to a deep blue one. Filter, wash, dry, and weigh the Prussian blue which is obtained.

Another Method.—Weigh out 5 grammes of red prussiate of potash (potassium ferricyanide) and 5 grammes of ferrous sulphate (copperas), and dissolve each in 100 c.c. of water; then mix the solutions.

The precipitate is filtered off, washed with water, dried, and weighed.

Third Method.—Weigh out 5 grammes of ferrous sulphate; dissolve in 100 c.c. of water, add 2 c.c. of nitric acid, and boil for half an hour. Then weigh out 5 grammes of yellow prussiate of potash, and dissolve in 100 c.c. of water; mix the two solutions. Filter off the precipitate of blue which is obtained, then wash, dry, and weigh it. Note that, as in the last experiment, a deep blue is at once obtained.

The blue pigment prepared by either of these processes can be tested in the following manner:—

1. Treat a little with hydrochloric acid, when it will be observed that no change is produced.

2. Boil a little in caustic soda, when the blue will be decomposed, and a brown precipitate of oxide of iron formed. Filter this off and wash the precipitate thoroughly, when it can be dissolved in hydrochloric acid and tested for iron.

To the filtrate add hydrochloric acid, then a solution of ferrous sulphate, when a blue precipitate will be obtained. This shows the presence of a ferrocyanide in the solution.

It may be mentioned here that the formation of a blue precipitate or colouration, on adding a solution of potassium ferrocyanide, is a test for iron. A test for the ferrocyanide is the production of a brown precipitate on adding copper sulphate.

Iron is one of these metals which form several distinct series of compounds; thus, with acids, it forms two series of salts, differing in composition, colour, and properties. One of these is the ferrous series in which the proportion of iron to acid is the largest; the ferrous compounds are characterised by having a green colour and by changing readily on exposure to the air. The other series of iron salts is the ferric, which are characterised by having an orange to red colour, and being fairly stable and permanent in character. By boiling the ferrous salts with

nitric acid, or treating them with chlorine, they are oxidised or changed into the ferric salts. The two series of iron salts give different results with the two prussiates (yellow and red) of potash :—

	Ferrous Salts.	Ferric Salts.
Yellow prussiate (ferrocyanide),	White precipitate,	Deep blue precipitate.
Red prussiate (ferricyanide),	Deep blue precipitate,	No precipitate, brown colour.

It will be observed that while in the first experiment a bluish-white precipitate is obtained, which becomes dark blue on being treated with the bleaching powder, in the second case a deep blue is got at once.

The composition of the two blues are quite distinct. Prussian blue is a compound of the elements iron, carbon, and nitrogen; the two latter are combined together in the form of a stable radicle called cyanogen, represented by the formula C N. The iron is really present in two forms—one basic, the other in combination with the cyanogen.

Potassium ferrocyanide has the formula $K_4 Fe C_6 N_6$, and potassium ferricyanide $K_3 Fe C_6 N_6$.

The precipitate obtained when potassium ferrocyanide and ferrous sulphate are mixed together consists of potassium ferrous ferrocyanide, $K_2 Fe Fe C_6 N_6$, and its production is shown in the next equation—

$$Fe S O_4 + K_4 Fe C_6 N_6 = K_2 S O_4 + K_2 Fe Fe C_6 N_6$$

The blue precipitate obtained when ferrous sulplate and potassium ferricyanide are mixed together is potassium ferrous ferricyanide, $K Fe Fe C_6 N_6$, and its formation is shown in the equation—

$$Fe S O_4 + K_3 Fe C_6 N_6 = K_2 S O_4 + K Fe Fe C_6 N_6.$$

This is sometimes called Turnbull's blue.

When potassium ferrocyanide and ferric sulphate are mixed together, a deep blue precipitate of potassium ferric ferrocyanide is obtained, having the formula $K_2 Fe\ 2 Fe C_6 N_6$, as represented in the equation—

$$Fe_2\ 3 S O_4 + 2 K_4 Fe C_6 N_6 = 3 K_2 S O_4 + K_2 Fe\ 2 Fe C_6 N_6.$$

Prussian blue and Turnbull's blue have exactly the same composition. They differ in the one being a ferrocyanide and the other a ferricyanide. The potassium they contain is rather difficult to eliminate; but when entirely eliminated, Prussian blue has the formula $Fe_7 C_{18} N_{18}$, while Turnbull's blue has the

formula $Fe_3 C_{12} N_{12}$. Prussian blue has usually a greenish tint, while Turnbull's blue has a violet-blue tint.

PROPERTIES OF PRUSSIAN BLUES.—Prussian blues are characterised by their deep greenish-blue tint; there is no other blue of the same depth of colour or of the same shade or tint. When dry they have a bronzy appearance, which is greatest when the blue is pure, and is especially characteristic of the variety known as Chinese blue.

They are very hard and exceedingly difficult to grind. For Prussian blue to develop its full colouring powers it is essential that it be ground as fine as possible. It is partly on account of this difficulty of grinding that Brunswick blue has come so largely into use, as painters are thereby saved the trouble of grinding.

Prussian blue is insoluble in dilute acids, and, usually, in strong hydrochloric acid (see below); boiling with nitric acid turns it of a greenish shade, while when boiled with strong sulphuric acid it is decomposed, sulphate of iron being formed, and hydrocyanic acid, &c., evolved. Some samples are insoluble in strong hydrochloric acid, others are soluble; much depends upon the process used in making and also upon the age of the sample; keeping seems to bring about some changes in the blue, whereby it is less easily soluble in the various agents which dissolve freshly-prepared blue readily enough.

Oxalic acid dissolves Prussian blue very readily; one part of oxalic acid will dissolve 8 to 10 parts of blue; such solutions have been used to make blue inks, but since the aniline colours came into commerce the use of Prussian blue for ink-making has decreased. By digesting insoluble Prussian blue at the ordinary temperature with the acid it is slowly converted into the soluble variety; on the other hand, if a solution in oxalic acid is boiled, the blue is gradually precipitated in the ordinary insoluble form; the same result can be brought about by the addition of sulphuric acid.

The most characteristic reaction of Prussian blue, which serves to distinguish it from other blues, is that when treated with any alkali, such as soda, potash, ammonia, or lime, it is decomposed into a ferrocyanide of the alkali and oxide of iron, the last being left behind as an insoluble residue having a red-brown colour, while the former passes into solution. Addition of acid in sufficient amount restores the blue colour, provided the ferrocyanide of the alkali formed has not been washed away. The Prussian blues and the pigments containing them cannot be used with alkaline vehicles, such as lime, whiting, silicate

of soda, or silicate of potash, as the blue would thereby be changed to red.

As a pigment Prussian blue is quite permanent and resists exposure to air, light, and most of the other atmospheric influences which act on pigments; it has, however, one curious property when used as a water colour, that of fading a little on exposure to light and of recovering its original intensity of colour in the absence of light.

Its colouring powers are very great, being by far the best of all the blues in this respect; $\frac{1}{2}$ oz. will tint 20 lbs. of white lead a perceptible blue. It is rather a transparent colour, so that its covering power is not great.

Heat decomposes it, the cyanogen it contains burns off as carbonic acid and nitrogen, while a blackish-brown or reddish-brown residue is left behind, according to the temperature to which it is exposed; a low temperature does not completely decompose it, and so a blackish-brown residue, consisting of a mixture of oxide of iron and carbon, is left behind; on the other hand, a high temperature causes all the carbon to be burnt off and a reddish-brown residue of ferric oxide to be left behind. In some cases this last residue may be a mixture of the two oxides of iron, ferrous and ferric, or it may be a mixture of ferric oxide and metallic iron; the result depends upon the conditions under which the blue is heated and its purity. The proportion of residue left depends upon the state of dryness of the blue, the process used in making it, and its purity; good qualities leave from 40 to 50 per cent. of residue.

Prussian blues can be mixed with nearly all other pigments without being affected or changed by them or affecting them in any way; the only exceptions are the few pigments of an alkaline character which destroy Prussian blue in the manner above described.

SOLUBLE BLUE.

For the manufacture of blue inks, laundry blues, &c., where a blue liquor is required, advantage is taken of the fact that Prussian blues can be prepared which are soluble in water or in oxalic acid.

PREPARATION OF SOLUBLE BLUE.—The ordinary Prussian blues are insoluble in water, as all pigments should be. There is, however, a variety which can be made that is soluble in water. There are several ways of preparing a soluble Prussian blue. The following is an interesting method :—Weigh out

5 grammes of perchloride of iron and 1 gramme of Glauber's salt, and dissolve in 70 c.c. of water. Then weigh out 10 grammes of yellow prussiate of potash and 1 gramme of Glauber's salt, and dissolve in 70 c.c. of water. Now pour the iron solution into the prussiate solution, collect the precipitate on a filter, and wash with water until the wash water comes through of a blue tint. Then dry the blues, which will be found soluble in water. It is important that the iron solution be poured into the prussiate solution, so that the latter is always in excess; the Glauber's salt takes no chemical part in the production of the blue, but it ensures the complete precipitation of the blue; for while the latter is soluble in pure water, it is not soluble in saline solutions, such as are formed when the Glauber's salt is used.

Oxalic acid and oxalates of the alkali metals have a solvent action on Prussian blue, and this is taken advantage of in making soluble blue. This is best done by first preparing the blue as described in the last experiment, then, when the blue has been filtered and got into the form of a stiff paste, 1½ grammes of oxalate of potash are stirred in, the whole dried, and then ground, when a powder will be obtained which is fairly soluble in water.

MANUFACTURE OF PRUSSIAN BLUES.—Commercially, several varieties of Prussian blue are made—viz., Chinese or bronze blue, Prussian blue, paste blue, and soluble blue. Of these the best and purest is Chinese or bronze blue, notable on account of the bronzy lustre which lumps of it show. While in the main the manufacture on the large scale follows on the lines laid down for the laboratory experiments, the following notes on the preparation of the blue for commerce will be of interest:—

PREPARATION OF CHINESE OR BRONZE BLUE.—There is required 2½ cwts. of yellow prussiate of potash of good quality, 2½ cwts. of green copperas, 10 gallons of sulphuric acid, and nitrate of iron made from 1½ cwts. of copperas and 3 gallons of nitric acid, boiled together. The process is as follows:—Dissolve the prussiate and copperas each separately in sufficient water, the more the better, run the prussiate solution into the large precipitating tank, then run in the copperas solution, boil the mixture for one hour, then add the sulphuric acid slowly and with constant stirring, boil for half an hour, then allow to stand for two days, next heat up to boil, add the nitrate of iron, stir well, allow to stand for six to eight hours, or all night, run through filter press, and wash the blue well with water. Then dry slowly at a gentle heat.

Another method of working is to proceed as above, but instead of adding nitrate of iron add 6 gallons of nitric acid and boil for three hours, then finish as before.

PRUSSIAN BLUE.—To make this, dissolve separately $1\frac{1}{4}$ cwts. of yellow prussiate of potash and $1\frac{1}{4}$ cwts. of green copperas; when both are dissolved run the prussiate solution into the bottom vat, then run in the iron solution, stirring well, next add 5 gallons of hydrochloric acid. There is next added 8 lbs. of bleaching powder dissolved to a thin cream in water in small quantities at a time. When all the bleaching powder or chloride of lime has been added, the mass is left to stand five to six hours, then it is run through the filter press, washed with water, and dried.

Another method of making is to take $1\frac{1}{2}$ cwts. of yellow prussiate and $1\frac{1}{2}$ cwts. of copperas; mix together as before; then add 5 gallons of sulphuric acid and 6 gallons of hydrochloric acid, boil with steam, then add 9 lbs. of bichromate of potash dissolved in 4 gallons of boiling water, stirring well, and allowing the mass to stand for some hours, then run through the filter press, wash, and dry.

Some makers add alum along with the copperas, but the blues so got are not of so fine a quality as those got with the iron salt only.

PASTE BLUE.—This is simply the Prussian blue not dried, it should contain 25 to 30 per cent. of actual blue.

SOLUBLE BLUE.—The methods of preparing this have been sufficiently indicated in the laboratory experiments detailed above.

ANTWERP BLUE.—This blue has practically gone out of use, having been replaced by the Brunswick blues. It is made by mixing 20 lbs. of copperas, 10 lbs. of alum, and 10 lbs. of zinc sulphate, with 60 gallons of water, and adding 40 lbs. of yellow prussiate of potash dissolved in 60 gallons of water; filtering, washing, and drying the pigment in the ordinary way.

Antwerp blue is paler than Prussian blue, owing to the alum and zinc it contains. Its properties as a pigment are practically identical with those of Prussian blue.

BRUNSWICK BLUE.

One trouble about the use of Prussian blue is that it is somewhat difficult to develop the full colouring power of the pigment. It is very troublesome to grind, and unless it is thoroughly ground its proper colour cannot be obtained, nor when used as

a staining colour is its full colouring power utilised. This, so far as the painter is concerned, can be got over by preparing what is known as Brunswick blue.

PREPARATION OF BRUNSWICK BLUE.—Weigh out 50 grammes of barytes and stir them thoroughly into 150 c.c. of water, then add 3 grammes of copperas (ferrous sulphate). Weigh out 3 grammes of potassium ferrocyanide (yellow prussiate of potash) and dissolve in 500 c.c. of water. When all is ready, mix the two solutions together, filter the blue which is formed, wash it with water, then dry it, and weigh. The tint of Brunswick blue may be varied by increasing or decreasing the proportion of the iron and potash salts.

Apply the following tests to the blue which is thus made:—Boil a little with caustic soda; it will be observed that the colour of the pigment turns brown, owing to the decomposition of the blue into oxide of iron; filter the residue thus got and wash it well with water.

Test the filtrate by adding hydrochloric acid and ferric chloride, when a blue precipitate will be obtained, showing the presence of a ferrocyanide. Treat the brown residue with hydrochloric acid, when a white residue of barytes will be left behind. This may be examined by the tests for barytes which will be found on another page. The solution which is obtained will give a blue precipitate on adding a solution of potassium ferrocyanide, showing the presence of iron.

MANUFACTURE OF BRUNSWICK BLUE.—The manufacture of Brunswick blue on the large scale follows on the lines shown in the laboratory method given above. It can be made of varying depths of shade from light to dark by using smaller or larger quantities of the prussiate and iron salts. For pale shades 1 cwt. of barytes, $1\frac{1}{2}$ lbs. of yellow prussiate, and $1\frac{1}{2}$ lbs. of copperas may be taken; for a deep shade 1 cwt. of barytes and 5 lbs. of each of the other salts. Sometimes ultramarine is added to the finished pigment.

PROPERTIES OF BRUNSWICK BLUE.—The properties of Brunswick blue closely resemble those of Prussian blue; it possesses better body or covering power on account of its containing barytes, but its staining power is much less.

ANALYSIS OF BRUNSWICK BLUE.—Sometimes it is desirable to ascertain the composition of Brunswick blues or other pigments which contain Prussian blue. Weigh out 3 grammes of the blue, boil with weak caustic soda lye until the blue is thoroughly decomposed, then filter and wash well with water, so as to free the residue from alkali. Next treat

the brown residue with hydrochloric acid to dissolve out the oxide of iron it contains, filter and wash with water, adding the first wash waters to the main filtrate. The white residue on the filter paper is now dried, placed in a weighed porcelain crucible, and heated over a Bunsen burner, then allowed to cool. On weighing it, the amount of the barytes will be obtained.

To the acid solution ammonia is added in slight excess to precipitate the oxide of iron, which is collected on a filter, washed, well dried, burnt in a crucible, and weighed. Multiplying the weight of the oxide of iron by 2·212 gives the weight of the Prussian blue present.

Other varieties of Prussian blue pigments may be tested in the same way.

BRUNSWICK GREEN.

Under a variety of names—Victoria green, chrome green, Brunswick green—green pigments in a large variety of shades are made and sold for house-painting. These are mixtures of Prussian blue, chrome yellow, and barytes; they are made by various processes, divisible into dry and wet methods.

PREPARATION OF BRUNSWICK GREEN.—The dry method of making these greens is often employed, and consists simply in grinding together barytes, Prussian blue, and chrome yellow on the small scale in a mortar; on the large scale in an edge runner mill.

The following proportions may be tried by the student:—

Pale Brunswick Green.

Barytes, ...	100 grammes.
Chrome yellow, ...	10 ,,
Prussian blue, ...	1½ ,,

Medium Brunswick Green.

Barytes, ...	100 grammes.
Chrome yellow, ...	10 ,,
Prussian blue, ...	3 ,,

Dark Brunswick Green.

Barytes, ...	100 grammes.
Chrome yellow, ...	10 ,,
Prussian blue, ...	5 ,,

Extra Deep Brunswick Green.

Barytes, ...	100 grammes.
Chrome yellow, ...	10 ,,
Prussian blue, ...	7 ,,

It will be noticed that the quantity of Prussian blue is increased in each recipe from "pale" to "extra deep," while those other constituents are kept constant. This is the main principle which underlies this method of making the various shades of Brunswick green.

The dry method has the advantage that with it it is easier to bring up the green to a standard tint, but the wet methods give the brightest shades.

Here, in making these greens, we depend on the principle that blue and yellow pigments when mixed together produce green, the exact tint of which depends upon the proportion of blue to yellow. When the latter predominates a yellow-green is got; when the blue is increased a blue-green shade is the result.

The wet processes consist essentially of producing the blue and yellow simultaneously, when they intimately unite and form the green. The materials used are barytes, lead acetate, bichromate of potash, yellow prussiate of potash (potassium ferrocyanide), and copperas (ferrous sulphate).

Wet Process.—Weigh out 50 grammes of barytes; mix in a convenient quantity of water; add to this 6 grammes of lead acetate and 1 gramme of copperas (ferrous sulphate). Also weigh out 1·75 grammes of potassium bichromate, and 1 gramme of yellow prussiate of potash; dissolve both together in 50 c.c. of water. When this solution is made, add it to the other mixture; the green forms immediately; it can be allowed to settle down to the bottom; it is then washed, filtered, and dried.

There will be thus obtained a pale Brunswick green. Other shades may be obtained in a similar manner by using other proportions of ingredients in such a manner that the proportion of Prussian blue increases with the depth of shade of the green, as, for instance, in the following recipes:—

Medium Brunswick Green.

Barytes,	50	grammes.
Lead acetate,	16	,,
Iron sulphate,	1·25	,,
Bichromate of potash,	1·75	,,
Ferrocyanide of potassium,	1·25	,,

Deep Brunswick Green.

Barytes,	100	grammes.
Lead acetate,	6·5	,,
Iron sulphate,	2·5	,,
Bichromate of potash,	1·75	,,
Ferrocyanide of potassium,	2·5	,,

Extra Deep Brunswick Green.

Barytes,	50	grammes.
Lead acetate,	7·5	„
Iron sulphate,	3·75	„
Potassium bichromate,	2·5	„
Potassium ferrocyanide,	3·75	„

Another Method.—Another plan of making these greens is to weigh out all the ingredients, as given above, in a mortar, and grind them together until they are thoroughly mixed, then pour on a quantity of water, and continue the grinding.

The green will rapidly form; it is then filtered off, washed well with water, and dried as usual.

Having made these Brunswick greens, the students should test them as follows:—

First, boil a little with caustic soda in a test tube and note any change of colour.

Second, boil a little with hydrochloric acid in a test tube and also note any change of colour.

The student should compare what has been already said as to the action of acids and alkalies on chrome yellow and Prussian blue with the results he finds on making these two tests.

MANUFACTURE OF BRUNSWICK GREEN.—The methods of working, employed in the small laboratory experiments and described above, are an epitome of the processes used on the large scale in making these greens, and so, beyond giving the quantities of materials which are used, it is not necessary to describe the processes in more detail in this book.

Dry Method.—A. Pale green. 1 cwt. of barytes, 1½ lbs. of Prussian blue, and 35 lbs. of chrome yellow.

B. Medium green. 1 cwt. of barytes, 2½ lbs. of Prussian blue, and 35 lbs. of chrome yellow.

C. Deep green. 1 cwt. of barytes, 5 lbs. of Prussian blue, and 35 lbs. of chrome yellow.

D. Extra deep green. 1 cwt. of barytes, 8 lbs. of Prussian blue, and 35 lbs. of chrome yellow.

Wet Process.—A. Pale green. 1 cwt. of barytes, 13 lbs. of acetate of lead, 1½ lbs. of copperas, 1½ lbs. of yellow prussiate of potash, and 4 lbs. of bichromate of potash.

B. Medium green. 1 cwt. of barytes, 13½ lbs. of acetate of lead, 2½ lbs. of copperas, 2½ lbs. of yellow prussiate of potash, and 4¼ lbs. of bichromate of potash.

C. Deep green. 1 cwt. of barytes, 14 lbs. of acetate of lead, 3 lbs. of copperas, 3 lbs. of yellow prussiate of potash, and 4½ lbs. of bichromate of potash.

D. Extra deep green. 1 cwt. of barytes, 6 lbs. of acetate of lead, 5 lbs. of copperas, 5 lbs. of yellow prussiate of potash, and 5 lbs. of bichromate of potash.

It may here be pointed out that, as thus made, the greens will contain some sulphate of lead formed by interaction between the lead acetate and copperas.

PROPERTIES OF BRUNSWICK GREENS.—They are good pigments, and work well both in oil and water, especially the former; their opacity is good, and, therefore, they have good body or covering power, in this respect surpassing all other green pigments. They can be mixed with other pigments, with but few exceptions, without any change being brought about by interaction; the exceptions comprise the pigments containing sulphur, which would act upon the chrome yellow and darken the green by the production of black lead sulphide; and highly basic colours, like whiting or lime, which would act both upon the chrome yellow, and the blue, turning the green into a red.

They are fairly permanent when exposed to light and air, for, although not quite permanent, they are so for all practical purposes; exposure to light causes the yellow constituent to fade first, as a rule, so that, especially in the dark shades, the green has a tendency to turn blue, but in this respect the blue is very variable; in some makes the yellow goes first, in others the blue; much probably depends upon the composition of the particular green and the circumstances under which it is placed.

Acids turn the colour bluer, owing to their dissolving out the chrome yellow; on the other hand, alkalies turn it orange, owing to their combined action both on the blue (turning this of a reddish-brown), and on the yellow (which they turn orange), as is noted in describing the blue and the yellow in their respective places. Sulphuretted hydrogen darkens the tint considerably.

It may happen that a quantitative analysis of Brunswick green is required. In that case the following hints will be found useful:—Weigh out 2 grammes of the green, boil well with hydrochloric acid, filter while hot, divide the filtrate into two equal portions, in one determine any sulphate of lead by precipitation with barium chloride, in the other determine the lead by precipitation with sulphuric acid, and the chromium by precipitation with ammonia. See what has been said about these tests under "Chrome Yellow."

Take the residue, which is insoluble in the acid, boil with caustic soda until all the blue is decomposed, then filter off the insoluble barytes, and weigh it; from the filtrate the iron is precipitated as hydroxide by adding ammonia, and this precipitate may be weighed. See under "Prussian Blue" for details of this test.

CHAPTER III.

PREPARATION OF PIGMENT COLOURS (*Continued*).

RED OXIDE.

THE red oxide of iron or ferric oxide, which has the chemical formula $Fe_2 O_3$, indicating that it contains 102 parts by weight of iron combined with 48 parts by weight of oxygen, forms the essential constituent of a number of red pigments known under the names of rouge, crocus, colcothar, Indian red, Venetian red, red ochre, purple oxide, Turkey red, &c.

Iron unites with oxygen to form four distinct oxides, or, to speak more correctly, its oxygen compounds can be traced to these four oxides as bases for them, although only two are capable of existing in the free condition. These oxides are—

1. Ferrous oxide or green oxide, $Fe O$.
2. Ferric oxide or red oxide, $Fe_2 O_3$.
3. Ferric anhydride, $Fe O_3$.
4. Ferric tetroxide, $Fe_3 O_4$.

The first is only known in the form of its hydroxide and the salts it forms, the ferrous compounds, with acid. The second occurs naturally in a variety of minerals; in combination with acids it forms the ferric salts.

The third oxide only occurs in combination with the alkalies, in the compounds known as ferrates.

The fourth oxide occurs naturally as magnetite, the natural loadstone or magnetic oxide of iron.

The last two oxides are of no importance in colour-making. The following experiments will demonstrate some of the properties of the ferrous and ferric oxides and their compounds, so far as their application to pigments is concerned :—

PREPARATION OF RED OXIDE (Rouge).—Weigh into a porcelain crucible 2 grammes of finely-powdered copperas (ferrous sulphate), and heat to a bright heat for some time over the Bunsen burner until a uniform red colour is obtained. Allow the crucible and its contents to cool, and then weigh. The weight will give the yield of this red which can be got from copperas.

Ferrous sulphate has the formula $Fe\,S\,O_4\,7\,H_2O$; on heating, the water of crystallisation it contains is driven off along with the sulphur trioxide in the form largely of sulphuric acid, but at the same time some oxidation occurs. This change is expressed by the chemical equation—

$$2Fe\,S\,O_4 \,.\, 7\,H_2O + O = Fe_2\,O_3 + H_2\,S_2\,O_7 + 13\,H_2O.$$

This reaction forms the basis for the preparation of many red pigments, as will be seen later on.

The red residue should be boiled with hydrochloric acid, when it will dissolve. Note that the solution has a strong yellow colour, and gives a brown precipitate with ammonia and a deep blue precipitate with potassium ferrocyanide. Both are characteristic reactions of ferric compounds.

PREPARATION OF FERROUS HYDROXIDE.—Dissolve 2 grammes of ferrous sulphate in water and add a slight excess of ammonia; filter off the precipitate that is obtained. Note the following points:—First, that a light green precipitate is obtained, which during filtration gradually turns red; second, that the filtrate tends to become turbid, and a reddish precipitate forms. This shows that the precipitation of ferrous sulphate by ammonia is not complete.

The reaction which occurs is represented by the equation—

$$Fe\,S\,O_4 + 2\,NH_4\,O\,H = Fe\,H_2\,O_2 + (N\,H_4)_2\,S\,O_4.$$

The ferrous hydroxide, $Fe\,H_2\,O_2$, which is precipitated in the form of a granular green mass, is not a stable body; it absorbs oxygen from the air, and gradually passes into ferric hydroxide, $Fe_2\,H_6\,O_6$—this change being indicated by a change of colour from green, the characteristic colour of ferrous compounds, to red, the characteristic colour of ferric compounds.

PREPARATION OF FERROUS CARBONATE.—Weigh out 5 grammes of ferrous sulphate (copperas), dissolve in 100 c.c. of water, and add a solution of sodium carbonate so long as a precipitate falls down. Warming the solution of copperas promotes the reaction and also quickens the subsequent filtration. Filter off the precipitate, wash the precipitate well on the filter, and dry it. Note that the green colour of the precipitate turns to red, indicating that, like the hydroxide, the ferrous carbonate is unstable and passes readily into the ferric compound. When the precipitate is dry, transfer as much as possible to a crucible, and heat to a bright red heat for a short time; then allow to cool, and weigh. The residue left is red, and consists of ferric oxide. Pigments have been made in this way.

The reactions which occur are expressed in the equations—

$$FeSO_4 + Na_2CO_3 = FeCO_3 + Na_2SO_4.$$
$$2FeCO_3 + O = Fe_2O_3 + 2CO_2.$$

PREPARATION OF RED OXIDE.–Weigh out 10 grammes of ferrous sulphate, and dissolve in 100 c.c. of hot water. Weigh out 2 grammes of good quicklime, and make into a milk with water. Mix the two solutions together; filter off any precipitate that is formed, wash with water, dry it, then transfer as much as possible to a crucible; heat over the Bunsen burner for a short time, allow to cool, and weigh. Note that the weight obtained is more than twice as much as is got from the last experiment, and that the same changes of colour are obtained.

The chemical reaction which takes place is shown in the equation—

$$FeSO_4 + CaH_2O_2 = FeH_2O_2 + CaSO_4.$$

Ferrous sulphate and calcium hydroxide (slaked lime) give ferrous hydroxide and calcium sulphate. Both the latter bodies are insoluble, and are precipitated together so that the final product obtained contains both ferric oxide and calcium sulphate. The red product should be kept and examined by the tests which will be given further on.

EXAMINATION OF FERROUS SULPHATE.—With the ferrous sulphate used in the above, the following experiments should be made:—

1. Dissolve a little in water and add a solution of potassium ferrocyanide (yellow prussiate of potash). Note that a white or faintly blue precipitate of ferrous ferrocyanide is got, and that, on filtering, this turns dark blue, because it changes into the ferric compound.

2. Dissolve a little in water and add a solution of potassium ferricyanide (red prussiate of potash). Note that a deep blue precipitate of ferrous ferricyanide is obtained.

3. Dissolve a little in water and add a solution of sulphocyanide of ammonia; no change will be noticed.

4. Dissolve a little in water and add a solution of caustic soda. Note the production of a green precipitate changing to red.

This result can be compared with that got when experimenting with ammonia and lime.

PREPARATION OF FERRIC SULPHATE.—Dissolve some ferrous sulphate in water, add a little nitric acid, and boil. Note the evolution of red fumes and the change of colour from

green to yellow. The nitric acid brings about an oxidation of the ferrous sulphate into ferric sulphate, which has the formula $Fe_2 3 S O_4$.

With this solution the following experiments may be carried out :—

1. Add a little potassium ferrocyanide. Note the deep blue precipitate of Prussian blue.

2. Add a little potassium ferricyanide. Note that no precipitate is produced and that the colour of the solution becomes a little darker.

3. Add a little sulphocyanide of ammonia. Note the deep red colour which is got.

The student should compare these results with the corresponding results obtained with the ferrous sulphate, as they are, first, characteristic tests for iron, and, second, distinguishing tests for the two classes of iron salts, the ferrous and the ferric.

4. Add to the solution a little ammonia. Note the brown-red colour of the precipitate of ferric hydroxide and its gelatinous character; and, further, that, on filtering, the filtrate is clear and colourless. These are characteristic of the ferric salts.

5. Add to the solution a little caustic soda. Note that the same precipitate is obtained as with ammonia.

6. Add to the solution a little ammonia and then a little ammonium sulphide. Note the formation of a black precipitate of the ferrous sulphide.

7. Add to the solution a little ammonia, filter off the precipitate and add to the filtrate, first, a little ammonium sulphide, and then a little ammonium carbonate. Note that no further precipitates are obtained.

Now dissolve the red residue obtained by adding lime and copperas together by boiling it in moderately strong hydrochloric acid. Divide the solution into two parts. One portion treat as above, and observe that on adding the ammonium carbonate a copious white precipitate indicative of the presence of lime is obtained. To the second portion add a little barium chloride, when a white precipitate of barium sulphate will be obtained. The precipitates with the ammonium carbonate and barium chloride show the presence of calcium sulphate in the red oxide which has been made.

PREPARATION OF VENETIAN RED. — Place 2 grammes of yellow ochre in a porcelain crucible and heat over the Bunsen burner to a bright red heat. Then allow the crucible to become cold, and weigh it. Note the loss of weight, which is chiefly moisture. Note that the colour of the residue

is red. The oxide of iron is present in the ochre in combination with water in the form of hydrated oxide, and this compound has a yellow colour; on heating, it loses water and turns to oxide, and the change is indicated by a change of colour.

The student may try the effect on the colour produced by heating yellow ochre for varying lengths of time, and observe that the longer it is heated the darker it becomes.

Ferric oxide occurs naturally in large quantities in the various forms of the mineral hæmatite, varying somewhat in form, hardness, &c. The mineral is one of the most valuable ones for the extraction of the metal, for, as a rule, it is fairly free from impurities. In an hydrated form—that is, combined with more or less water—it forms the mineral limonite, which has a brown colour and is the form in which the oxide is found in yellow ochres, siennas, umbers, &c.

MANUFACTURE OF NATURAL OXIDE REDS.—Although ferric oxide is an abundant mineral found in numerous places on or in the earth, yet there are few of these deposits which are capable of being used as pigments for paint making. When such are met with all that is necessary is to grind them up in an edge runner grinding and levigating mill with water to remove any grit, settling in levigating tanks, and drying.

The following analyses give some idea of the composition of natural reds:—

Cumberland Red.

Ferric oxide, Fe_2O_3,	96·00 per cent.
Alumina, Al_2O_3,	1·24 ,,
Silica, SiO_2,	1·41 ,,
Water,	1·35 ,,

Red from India.

Ferric oxide, Fe_2O_3,	94·38 per cent.
Alumina, Al_2O_3,	1·60 ,,
Silica, SiO_2,	2·80 ,,
Calcium carbonate, $CaCO_3$,	0·39 ,,
Water, combined,	0·69 ,,
Water, hygroscopic,	0·14 ,,

MANUFACTURE OF ROUGE.—Under the names of rouge, colcothar, crocus, &c., there are sold large quantities of red prepared from copperas (ferrous sulphate).

Copperas contains some water of crystallisation, and has the formula $FeSO_4 7H_2O$; most of this water is given off at a gentle heat. If the dried copperas be subjected to a strong red heat in an iron still or in a muffle furnace it loses all its sul-

phuric acid and a residue of oxide of iron is left behind, usually as a bright red powder. At one time this was the operation employed for obtaining the sulphur compounds as Nordhausen or fuming sulphuric acid, and so the red oxide was a bye-product, but it is seldom used for this purpose now.

Some fine reds are made by thus heating copperas; by adding a little salt to it, still finer reds are produced. After being heated it is necessary to wash the red with water (to remove all traces of soluble salts and acid), then to filter and to dry it.

Generally these reds consist of pure oxide of iron; they have a bright colour, and are strong in staining or colouring power.

MANUFACTURE OF VENETIAN RED.—This important red pigment is made by heating yellow ochre in a crucible or muffle furnace for some hours until a little taken out shows that it has acquired the right tint.

Some makers produce it by mixing red oxide, yellow ochre, barytes, and whiting together, but such mixtures are not so good as pigments as those made from yellow ochre.

Venetian red has a pale red colour; it possesses fairly good covering power of body, although much depends upon the character of the ochre used in making it. It is used in all kinds of house painting, as, like all oxide of iron reds, it is quite permanent.

The composition of Venetian red depends upon that of the ochre or mixture of pigments from which it is made.

The following analysis of a sample of Venetian red will give some idea of its composition:—

Water,	1·25	per cent.
Oxide of iron, Fe_2O_3,	20·70	,,
Alumina, Al_2O_3,	25·35	,,
Silica, SiO_2,	39·40	,,
Calcium carbonate, $CaCO_3$,	8·64	,,
Calcium sulphate, $CaSO_4$,	4·66	,,

MANUFACTURE OF RED OXIDE.—Under the name of red oxide and various other names are sold pigments of a a dark red colour varying considerably in brilliance, depth of shade, and staining or colouring power. They are darker in colour and stronger pigments than the Venetian reds, but not so dark in colour as the Indian reds. They are now almost entirely made from the waste iron liquors which are produced in various metallurgical processes—extraction of copper from pyrites, galvanising iron goods, &c. Some of these liquors contain the iron as ferrous chloride, others as ferrous sulphate. The general method of procedure is to add lime to the liquors in

sufficient quantity to throw down all the iron; an excess of lime must be avoided. When the liquors consist of ferrous chloride only, then the precipitate will consist of ferrous hydroxide only with, perhaps, a little carbonate of lime; when the liquors contain ferrous sulphate, then the precipitate will contain ferrous hydroxide and calcium sulphate. The finished pigment will in the one case consist of ferric oxide almost entirely, in the other of a mixture of ferric oxide and calcium sulphate.

After precipitation the mass is filtered, washed, dried, and then heated in a muffle furnace to a red heat. The tint of the finished product depends upon the degree and duration of the heating. After the furnacing, the pigment is ground before it is sent out for sale.

These oxide reds are usually of good quality and strong in colouring or staining power; they have good body or covering power, and are useful for all kinds of painting work.

Their composition will vary according to their method of making (as already pointed out), or to the nature of the additions, as whiting or barytes, made to the finished product in order to bring it up to a special shade.

The following analyses give some idea of their composition:—

	1.	2.	3.
Ferric oxide,	43·59	30·59	80·68
Calcium sulphate,	53·94	53·60	5·28
Water,	2·35	15·75	5·18
Calcium carbonate,	...	...	17·73
Magnesia,	·12	·06	1·13

MANUFACTURE OF INDIAN RED.—The original Indian red was a natural hæmatite of a dark red colour found in India, but a great majority of the Indian reds now on the market are made by strongly heating ochres, iron precipitates, &c., until they acquire the desired deep red shade commonly known as Indian red.

In general properties as pigments they resemble the other oxide reds, and so nothing further need be said here.

The composition of Indian red varies considerably according to the source of the raw material. The following are some analyses of various commercial Indian reds:—

Natural Indian Red.

Oxide of iron,	94·71	per cent.
Alumina,	1·60	,,
Silica,	2·80	,,
Calcium carbonate,	0·39	,,
Water,	0·50	,,

Indian Red from Waste Iron Liquors.

Ferric oxide, ...	43·59 per cent.
Calcium sulphate, . . .	53·94 ,,
Alumina, ...	1·05 ,,
Water, ...	1·42 ,,

Indian Red from Derbyshire Ochre.

Ferric oxide, ...	63·91 per cent.
Alumina, ...	0·60 ,,
Calcium carbonate, . . .	3·31 ,,
Barium sulphate, . . .	21·11 ,,
Water, ...	10·65 ,,
Magnesia, ...	0·42 ,,

Manufactured Indian Red.

Ferric oxide, ...	92·72 per cent.
Silica, ...	1·36 ,,
Calcium sulphate, . . .	5·52 ,,
Water, ...	0·40 ,,

MANUFACTURE OF PURPLE OXIDES.—Purple oxides are pigments of a very dark bluish-red colour ; they are often made from the residual oxide of iron left in the process of making sulphuric acid from pyrites by grinding and levigating in water. Or they are made by the same process as making red oxide, only the heating in the furnace is carried on longer and at a higher temperature. Usually they consist of ferric oxide only, as will be seen from the following analysis :—

Ferric oxide, ...	98·5 per cent.
Silica, ...	1·2 ,,
Water, ...	0·3 ,,

PROPERTIES OF IRON OXIDE REDS.—Red oxide pigments form red powders of various shades, from a pale red to a dark violet, the specific gravity of which varies from 2·6 to 3·1 ; they are quite insoluble in water, and more or less insoluble in acids. If the oxide has been made at a low temperature, as, for instance, rouge, it will dissolve fairly readily in strong hydrochloric acid ; if it has been made at a higher temperature, Indian red for example, it is not readily soluble in hydrochloric acid, and requires a mixture of that acid and nitric acid to effect its solution ; while the purple oxides which have been prepared by calcining at a very high temperature are very insoluble bodies, and require to be treated with a mixture of sulphuric, hydrochloric, and nitric acids before they will dissolve. This point regarding the solubility of oxide reds should be borne in mind when making an analysis of these bodies. Of course, it is only

the pure oxides which are soluble; those made from ochres always yield an insoluble residue of some kind.

As a pigment red oxides are perfectly permanent under all conditions, and are among the most permanent pigments a painter can use. They mix perfectly with all pigments without either affecting them in any way or being affected by them. They do not mix so well with oil as red lead, and take about 10 per cent. of oil to grind into the usual stiff paste; they do not act as driers.

ANALYSIS OF IRON OXIDE PIGMENTS.—From what has been said as to the methods of preparation of red oxides, it will have been gathered that these bodies are of very variable composition. Some are nearly pure oxides, others contain calcium sulphate; while others are much more complex, containing silica, alumina, calcium carbonate, &c. In technical work it is rare that the absolute purity of a body is an essential feature, and this applies, as a rule, to these pigments particularly; with them this character will not affect the use of the pigment as a pigment. It is rarely, therefore, that an analysis of a red oxide is required.

When an analysis is required of an oxide red, the following scheme may be adopted :—

Water.—Weigh 2 grammes into a watch-glass, and heat in a hot oven to a temperature of about 120° C. until there is no further loss of weight. This gives the hygroscopic water. For the combined water weigh 2 grammes into a crucible, and heat to a red heat over the Bunsen burner for about one hour; then, after allowing to cool, weigh. The loss of weight is the hygroscopic *plus* the combined water.

Next weigh into a beaker 5 grammes, and heat with a mixture of hydrochloric and nitric acids until the red is completely decomposed; then evaporate the solution to dryness, treat the dry mass with a little dilute hydrochloric acid, filter off into a 500 c.c. flask, wash well with water, and fill the flask up to the mark. The residue on the filter is the silica, barytes, &c., which can be dried and weighed.

For the iron, alumina, &c., take 200 c.c. of the above solution, add carbonate of soda until the solution is neutral, then ammonium acetate; boil, filter, wash and dry, and weigh the precipitate. This consists of oxide of iron, alumina, and, in some rare cases, phosphoric acid, but this may be neglected, as a rule, in iron reds. The iron may be estimated in another portion of the original solution by a volumetric test and the amount of alumina calculated from the two results. The filtrate from the

precipitate is mixed with a small quantity of ammonium sulphide to precipitate manganese, this precipitate being collected, dried, and weighed. To the filtrate is added ammonium oxalate to precipitate the calcium, which is filtered off, dried, and weighed. To the filtrate from this, sodium phosphate is added to precipitate the magnesium, if present.

For the sulphate which is present 100 c.c. of the original solution are taken, and some barium chloride is added; the precipitate of barium sulphate is filtered off, dried, and weighed.

For fuller details as to the method of carrying out this scheme, works on quantitative analysis, such as that of Professor A. H. Sexton, published by Griffin & Co., should be consulted.

YELLOW OCHRE.

Yellow ochre is a natural pigment found in the form of bright yellow, earthy masses in many places scattered over the world. In England it is found in the counties of Oxford, Derby, Gloucester, Devon, and Cumberland; in Wales, Merionethshire, Carnarvonshire, and Anglesea; and it is also found in Ireland, France, Scotland, Germany, Canada, United States, Australia, and South Africa.

The mineral is dug out, ground up with edge-runner grinding mills, and then subjected to a process of levigating to separate out coarse and gritty particles, and finally dried before sending on to the market for sale.

The colour and quality of yellow ochre vary very much, from a bright golden yellow in the case of the Oxford ochre to a dull brownish-yellow in the case of Derbyshire and American ochres. Some ochres are strongly, others weakly, coloured.

In chemical composition ochres vary very much, depending partly upon the rock formation in which they are found, so that there is no recognised standard. The essential feature to which they owe their colour is the presence of limonite, a hydrated oxide of iron, and this is mingled with alumina silicate, lime, barytes, &c.; but the value of an ochre does not depend so much upon the amount of this iron compound which may be present as upon its physical condition and how it is united with the other ingredients which are present. The following analyses of ochre made by the writer show some typical examples, and how these vary from one another:—

1. Oxford Ochre.

Water, hygroscopic,	6·88	per cent.
Water, combined,	8·15	,,
Calcium oxide, CaO,	0·99	,,
Sulphur trioxide, SO_3,	1·32	,,
Alumina, Al_2O_3,	6·47	,,
Ferric oxide, Fe_2O_3,	12·81	,,
Silica, SiO_2,	63·48	,,

2. Welsh Crude Ochre.

Water, hygroscopic,	2·00	per cent.
Water, combined,	12·50	,,
Sulphur trioxide, SO_3,	1·31	,,
Silica, SiO_2,	29·72	,,
Alumina, Al_2O_3,	33·31	,,
Ferric oxide, Fe_2O_3,	20·70	,,
Copper sulphide, CuS,	0·51	,,

3. Derbyshire Ochre.

Water, combined,	6·10	per cent.
Barium sulphate, $BaSO_4$,	20·94	,,
Silica, SiO_2,	4·53	,,
Calcium sulphate, $CaSO_4$,	2·51	,,
Calcium carbonate, $CaCO_3$,	21·75	,,
Alumina, Al_2O_3,	10·65	,,
Ferric oxide, Fe_2O_3,	33·49	,,
Magnesia, MgO,	trace.	

4. French Ochre.

Water, hygroscopic,	1·8	per cent.
Water, combined,	9·2	,,
Silica, SiO_2,	54·00	,,
Alumina, Al_2O_3,	13·7	,,
Ferric oxide, Fe_2O_3,	20·7	,,
Calcium oxide, CaO,	0·1	,,

5. American Ochre.

Water, hygroscopic,	1·3	per cent.
Water, combined,	3·7	,,
Ferric oxide, Fe_2O_3,	11·0	,,
Alumina, Al_2O_3,	4·0	,,
Silica, SiO_2,	4·4	,,
Calcium carbonate, $CaCO_3$,	trace.	
Barium sulphate, $BaSO_4$,	75·3	,,

PROPERTIES OF OCHRES.—So far as their properties as pigments are concerned, the ochres rank among the most permanent pigments at the disposal of the painter. They are unaffected by admixture with any other pigments, do not act

injuriously upon other pigments, and are scarcely affected by exposure to the atmosphere and its destructive influences. They work well with all kinds of vehicles, and can, therefore, be used in any kind of painting — oil, water, distemper, fresco, &c.

Ochres vary very much in tint, brightness of colour, and strength.

Oxford ochre is the brighest of the ochres and is of a fairly bright brownish-yellow colour. Welsh ochres are rather duller than Oxford ochres, French ochres are moderately bright, Derbyshire ochres are reddish in tone and are darker than other varieties of ochre. They vary very much in texture. Oxford ochre is of a soft texture; some are gritty in feel, while others have a clayey feel. In body or opacity this pigment varies very much. The Oxford ochre is rather transparent, and is commonly used as a glazing colour; the other ochres are more opaque and have good body; hence they are largely used as body colours, especially in house painting.

The colour of ochre is due to the presence of hydrated peroxide of iron; the shade or tint depends mainly upon the proportion of iron present, and also, but to a less extent, upon the degree of hydration of the oxide of iron; in proportion as the iron oxide is less and the hydration greater, the yellower and brighter the shade of colour; when the proportion of non-hydrated oxide of iron is large the shade becomes redder.

When ochres are treated with hydrochloric acid, the iron they contain is nearly all dissolved out, and yields a yellow solution which will give the characteristic test for iron, while a more or less insoluble residue is left behind.

Heat turns ochres a red colour, the shade of which depends upon the temperature and length of time the heating is carried on; these red colours are sold as Venetian red, light red, Indian red, &c.; their preparation and properties have already been described.

This change of colour is due to the passage of the iron oxide from the hydrated to the anhydrous condition.

ANALYSIS OF OCHRES.—The crude ochres should be first tested for the actual quantity of colour present. A tall glass of a conical shape is provided; a glass funnel with a long stem passes down to the bottom of the glass, into which is put about 25 to 30 grammes of the crude ochre; into the glass is now passed a gentle current of water sufficiently strong to carry out of the glass all the finer particles of colour, while leaving the heavier and more gritty particles behind, which are collected

by filtering and, after drying, are weighed in the usual way. From the weight is calculated the proportion of colour and grit. Thus, a sample of crude Irish ochre, tested in this way, was found to contain—

Grit, ...	30·24 per cent.
Colour, ...	69·76 ,,

PREPARED OCHRES.—It is rarely that an analysis of ochres is required; but analyses of several varieties are given above, which show their constituents and what to look for in analysing them. Ochres are rarely, if ever, adulterated. Ochres which are naturally poor in colour sometimes have a little chrome yellow added to them to bring up the tint; such an addition may be recognised by treating the ochre with hydrochloric acid and alcohol, when a green-coloured solution containing chromium will be obtained, the chromium in which may be detected by the usual tests.

LABORATORY WORK WITH OCHRES.

Ochres, siennas, and also umbers, being natural pigments, do not permit of much laboratory work being done with them.

HUE AND TINT.—These pigments vary very much in their hue or tone of colour, and the student would do well to compare together several samples of ochres, as also siennas and umbers, from different localities.

One should be taken as a standard and the rest compared with it. To do this, place a sheet of dead black paper on a table in front of a window, but not in direct bright sunshine; diffused light is the best. Then by means of a palette knife, a small heap of the standard sample is placed on the paper and by its side a similar heap of the other sample to be compared with it, and then by a firm but steady pressure the heaps are flattened down to a smooth surface, care being taken not to mix the two heaps. Now observations are made as to the relative strength of colour of the two samples, which is the deeper or paler of the two, also whether one is of a different hue or tint to the other—that is, whether it is either redder or browner, or more of a true yellow than the other.

STRENGTH OF COLOUR.—Sometimes one ochre has more colouring or staining power than another ochre. This is determined in the following manner:—5 grammes of each sample of ochre are mixed with 15 grammes of china clay, the mixture being carefully done on a sheet of paper. Then the tint of the

two mixtures are compared together in the manner just described; the ochre in the mixture having the deepest tint has the most colouring power. To get an indication of the relative strength of the two samples the following procedure is adopted:—To the more deeply tinted mixture small weighed quantities, say 2 grammes, of china clay are added until both mixtures have the same tint; the amounts of china clay used in the two samples are a measure of the relative strength of the samples; thus, for instance, one sample of ochre required 15 grammes of china clay, another 19 grammes, and a third 21 grammes to bring them all down to the same tint; the ratio of strength of colouring power is, therefore, as 15 : 19 : : 21, or, if the strongest is taken as 100, then the proportion sums 21 : 19 :: 100, and 21 : 15 :: 100 give, in percentages, the relative strength as 100, 90·47, and 71·42.

Heat 2 grammes of ochre in a porcelain crucible in a hot oven at 100° C. for two to three hours and then weigh. The loss of weight gives what is called the hygroscopic moisture in the sample. Then place the crucible over the Bunsen burner, heat to a bright red heat for half an hour, allow to cool, and weigh again. The loss of weight represents the water which was present in the ochre in a state of chemical combination with the iron, &c. Note that the colour is changed to red. This is characteristic of ochres and siennas.

Heat some ochre for some time with strong hydrochloric acid in a test tube. Note that, as a rule, the yellow colour disappears and a white residue is obtained. This may consist of silica, barytes, or some other insoluble constituent of the ochre. The same experiment may be tried with the red product obtained by heating the ochre and the observation be made that it is more difficult to dissolve than the original yellow ochre. In fact, the longer it is heated and the higher the temperature to which it is subjected the less soluble it becomes. This is a characteristic property of the oxides of iron, alumina, and chrome which should not be forgotten when making analysis of these bodies.

To the acid solution add a little ammonia, when a pale reddish-brown precipitate will be obtained, which shows the presence of both iron and alumina. Filter this off and add a few drops of ammonium sulphide to the filtrate, when, if manganese be present, a brownish precipitate will be obtained. Filter this off and add ammonium carbonate to the filtrate, when a white precipitate of calcium carbonate will be obtained, if lime be present in the ochre.

All the above experiments can be applied to siennas, umbers, and all natural yellow and brown pigments, as well as to ochres.

SIENNAS.

Siennas very closely resemble the ochres in many respects. They owe their colour to limonite, but also contain a little manganese and some organic matter; they are browner in hue and less opaque than ochres. They are natural products, and were originally found near the town of Sienna in Italy, to which circumstance they owe their name. Although now found in many other places, Italian siennas still command the best prices. The siennas are found in deposits of various extent, and are simply dug out, levigated to free them from grit, dried, graded into various qualities according to tint, and then put on the market.

Two kinds of sienna are used in the paint trade—Raw Sienna and Burnt Sienna.

Raw sienna is the yellow product as found and prepared for use in the manner indicated above. In colour it is brownish-yellow, somewhat more transparent than yellow ochre, but otherwise identical in properties.

The following analyses of Italian sienna will show the substances usually found in them :—

Italian Sienna.

Water, hygroscopic, . . .	17·55	per cent.
Water, combined, and organic matter,	9·00	,,
Silica, SiO_2, ...	22·65	,,
Calcium carbonate, $CaCO_3$, . .	0·96	,,
Alumina, Al_2O_3, . . .	2·84	,,
Manganese, Mn_2O_3, . . .	1·19	,,
Ferric oxide, Fe_2O_3, . . .	45·82	,,
Magnesia, MgO, . . .	...	

American Sienna.

Water, hygroscopic, . . .	7·00	per cent.
Water, combined, . . .	6·20	,,
Iron oxide, Fe_2O_3, . . .	74·81	,,
Alumina, Al_2O_3, . . .	5·23	,,
Manganese, Mn_2O_3, . . .	trace.	
Lime, CaO, ...	trace.	
Silica, SiO_2, ...	6·76	,,

BURNT SIENNA.

The siennas are sold in two forms—raw and burnt; the first has already been dealt with, and the latter will now be described.

Burnt sienna is prepared by calcining the raw sienna at a moderate red heat until it has acquired the desired shade. The tint of burnt sienna depends not only upon the temperature used and the length of time it is exposed to heat, but also upon the shade of the raw sienna used. Burnt sienna is a pigment of a reddish-orange shade, very similar to that of the coal-tar colour known as Bismarck brown. It is very transparent, and is, therefore, mostly used as a glazing or tinting colour by painters and artists. It is sold in the form of small pieces, and of a paste ground up with water or oil. The former variety is very difficult to grind.

The composition of burnt sienna naturally resembles that of raw siennas, but the heat has driven off most, if not all, the water the latter contained. The following analysis will serve to show the composition of Italian burnt sienna:—

Water, hygroscopic,	9·45	per cent.
Water, combined,	3·27	,,
Silica, SiO_2,	36·91	,,
Calcium carbonate, $CaCO_3$,	1·23	,,
Manganese, Mn_2O_3,	traces.	
Alumina, Al_2O_3,	3·48	,,
Ferric oxide, Fe_2O_3,	45·65	,,

The whole of the water in this sample had not been driven off by the burning.

A sample of American burnt sienna had the following composition:—

Water, hygroscopic,	2·60	per cent.
Water, combined,	2·10	,,
Ferric oxide, Fe_2O_3,	89·13	,,
Alumina, Al_2O_3,	2·53	,,
Silica, SiO_2,	4·56	,,
Manganese and lime,	traces.	

Why raw siennas should give an orange-red pigment on calcining and ochres a red is somewhat uncertain; probably the fact that siennas contain organic matter, and that the iron is in both the ferrous and ferric conditions, may have some influence.

UMBER.

This is a natural brown pigment found, like the ochres, in many places, as in Derbyshire, Devonshire, Cornwall, and Wales in this country; in France, Italy, and North America. The most esteemed is that from the Isle of Cyprus, generally known as Turkey umber, because it finds its way to this country through Turkey.

COMPOSITION OF UMBERS. — In composition the umbers resemble the ochres and siennas, but differ in containing more manganese. The following analyses of various umbers show their usual composition :—

Cyprus Umber.

Water, hygroscopic, . . .	4·32 per cent.
Water, combined, . . .	8·45 ,,
Silica, $Si O_2$, ...	29·56 ,,
Calcium carbonate, $Ca C O_3$, . .	5·56 ,,
Manganese, $Mn_2 O_3$, . . .	12·28 ,,
Alumina, $Al_2 O_3$, . . .	2·73 ,,
Ferric oxide, $Fe_2 O_3$, . . .	36·47 ,,

Derbyshire Umber.

Water, hygroscopic, . . .	13·47 per cent.
Water, combined, . . .	5·17 ,,
Silica, $Si O_2$, ...	4·43 ,,
Calcium carbonate, $Ca C O_3$, . .	2·60 ,,
Manganese, $Mn_2 O_3$, . . .	11·53 ,,
Alumina, $Al_2 O_3$, . . .	8·07 ,,
Ferric oxide, $Fe_2 O_3$, . . .	22·50 ,,
Barium sulphate, $Ba S O_4$, . .	30·10 ,,
Calcium sulphate, $Ca S O_4$, . .	2·15 ,,
Phosphoric acid, . . .	trace.

Devonshire Umber.

Water, hygroscopic, . . .	6·61 per cent.
Water, combined, . . .	10·25 ,,
Silica, $Si O_2$, ...	24·51 ,,
Calcium carbonate, $Ca C O_3$, . .	6·09 ,,
Manganese, $Mn_2 O_3$, . . .	7·11 ,,
Alumina, $Al_2 O_3$, . . .	12·80 ,,
Ferric oxide, $Fe_2 O_3$, . . .	29·98 ,,
Calcium sulphate, $Ca S O_4$, . .	2·13 ,,

Umbers are pigments of a warm brown colour, varying in hue from yellowish to violet-brown. By calcining, the colour is rendered darker and warmer. As pigments they work well in both oil and water, and they can be mixed with all other

pigments without any change occurring. They are perfectly permanent, being unaffected by all the ordinary conditions to which pigments are exposed. Umbers, therefore, meet with extensive use among all classes of painters. Umbers sold in the same condition as extracted are called "raw umbers," those which have been heated as "burnt umbers."

Umbers are not readily attacked by acids, but prolonged digestion with strong hydrochloric acid dissolves the larger proportion of the umber, forming a brownish-yellow solution containing iron, alumina, manganese, and lime; the silica and the barium sulphate remain undissolved. The metals may be tested for by the usual analytical methods. Caustic soda has no action on umbers.

CHAPTER IV.

PREPARATION OF PIGMENT COLOURS (*Continued*).

THE white pigments occupy an important position in the preparation of paints, for they have often a double part to play; first, they not only give colour to the paint (as do such pigments as chrome yellow, Prussian blue, Brunswick green), but, second, they also act as "body" colours; that is, they impart to the paint the degree of opacity required to enable the paint to cover or hide the surface to which it is applied, a function which coloured pigments are not, as a rule, called upon to perform. There are many white pigments (white lead, zinc white, barytes, &c.), but, in the opinion of painters, the premier position is assigned to white lead.

WHITE LEAD.

Manufacturers have tried numerous processes for its preparation, details of which will be found in the author's *Manual of Painters' Colours*, but few of them are in actual use by them. The most important is the Dutch process, but as this is not suited for experimental practice by the student, the chemical composition and properties of the pigment will be illustrated by methods which can be carried out in the laboratory.

PREPARATION OF WHITE LEAD.—(*a*) Weigh out 10 grammes of acetate of lead and $7\frac{1}{2}$ grammes of soda crystals; dissolve each separately in 150 c.c. of water; when the solutions are ready, pour that of the soda into the lead solution. A white precipitate is obtained which can be filtered off, washed, dried, and weighed.

The reaction which takes place is represented in the following equation—

$$\underset{\text{Lead acetate.}}{Pb2C_2H_3O_2} + \underset{\text{Sodium carbonate.}}{Na_2CO_3} = \underset{\text{Lead carbonate.}}{PbCO_3} + \underset{\text{Sodium acetate.}}{2NaC_2H_3O_2},$$

from which we see that there are formed lead carbonate and sodium acetate, the former as a precipitate, while the latter remains in solution. The equation is based on the supposition that the normal lead carbonate is formed. By normal lead

carbonate is meant the salt formed by the union of equivalent quantities of lead oxide, $Pb\,O$, and carbonic acid, $C\,O_2$, having the formula $Pb\,C\,O_3$, but there is reason for thinking that the normal lead carbonate cannot be made by precipitating. What is really formed is a basic carbonate; that is, a compound in which there is more than an equivalent quantity of the base, $Pb\,O$, either in the form of oxide or hydroxide, which may have the formula $Pb\,(Pb\,O)\,C\,O_3$ or $Pb\,(Pb\,H_2\,O_2)\,C\,O_3$; or there might even be the compound $Pb\,(2\,Pb\,O)\,C\,O_3$. We are not yet sufficiently familiar with what actually does take place when a solution of sodium carbonate is added to one of lead acetate. There is good reason for thinking that the actual result is modified by such circumstances as strength of solutions, temperature, &c.

This is the simplest method, but it is one which is not used on the large scale, because it is found that the precipitate has a crystalline structure which, as will be seen presently, is fatal to its possession of good qualities as a pigment.

(*b*) Weigh out 10 grammes of lead acetate, dissolve in 150 c.c. of water, add to the solution $3\frac{1}{2}$ grammes of powdered litharge, and boil for some time. The litharge will almost entirely dissolve; filter the solution from any undissolved litharge, and pass a current of carbonic acid gas through the filtrate. A white precipitate of carbonate of lead will be thrown down, which may be filtered off, washed, and dried. The carbonic acid is conveniently obtained by acting with hydrochloric acid on marble placed in a bottle through the cork of which a glass tube passes (see Fig. 7), the gas being conducted through an indiarubber tube into the solution of lead.

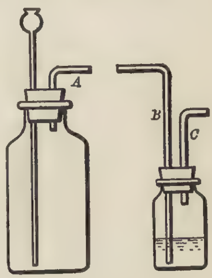


Fig. 7.

By boiling the lead acetate and the litharge together, the latter dissolves, forming a basic acetate of lead, as shown in the equation—

$$\underset{\text{Lead acetate.}}{Pb\,(C_2\,H_3\,O_2)_2} + \underset{\text{Litharge.}}{2\,Pb\,O} + \underset{\text{Water.}}{2\,H_2\,O} = \underset{\text{Basic acetate of lead.}}{2\,(Pb\,H_2\,O_2)\,Pb\,(C_2\,H_3\,O_2)_2}.$$

Now, when the carbonic acid gas is passed through, the dissolved litharge is thrown down as basic carbonate of lead, as shown in the equation—

$$\underset{\text{Basic lead acetate.}}{Pb(Pb\,H_2O_2)_2(C_2H_3O_2)_2} + \underset{\text{Carbonic acid.}}{CO_2} = \underset{\text{Basic lead carbonate.}}{Pb(Pb\,H_2O_2)CO_3} + H_2O + \underset{\text{Lead acetate.}}{Pb(C_2H_3O_2)_2}.$$

Here again it is found in practice that the actual composition of the precipitate which is obtained is dependent upon the strength of the solution used, temperature, &c., and, although processes have been devised for making white lead on a large scale in this way, they have not been a great success. It will be noticed that lead acetate is again formed. This may be used over again for making more of the solution of basic lead acetate.

The French process and Cory's process are based on this method of working.

PREPARATION OF WHITE LEAD.—Weigh out 13 grammes of lead acetate and 8 grammes of litharge; stir both in 200 c.c. of water, then boil the mixture until the litharge is dissolved or a white residue is obtained; a little water may be added from time to time as the original water boils away.

Now add a solution of 6 grammes of sodium carbonate in 100 c.c. of water; the white lead is precipitated out, and can be filtered, washed, dried, and weighed.

This method has been followed on the large scale, as in Condy's process, but the results have not been altogether satisfactory.

The above represent all the processes which, without the construction of special appliances, the student can use to prepare white lead.

Having got white lead by one or other of these processes, the student should proceed to test it as follows:—

1. Place a little in a test tube with dilute pure nitric acid. Note that it dissolves with effervescence.

2. Place a little in a test tube with pure acetic acid. Note that it dissolves with effervescence.

3. Boil with a little hydrochloric acid. Note that it dissolves with effervescence, but that when the solution cools, transparent crystals of lead chloride separate out. This is a very characteristic test for lead, and serves to distinguish white lead from whiting.

4. Boil a little with sulphuric acid. Note that, while there is some effervescence, no solution takes place; the white lead is changed to sulphate of lead, which is insoluble.

5. Add potassium bichromate to the acetic acid solution. Note the yellow precipitate which is obtained.

6. Add sulphuric acid to the nitric acid solution. Note the white precipitate of lead sulphate which is obtained.

7. Add ammonia to the acid solution. Note the white precipitate of lead hydroxide which is obtained.

To the acid solution add a little ammonia to just neutralise

any acidity and then a few drops of ammonium sulphide, when a black precipitate of lead sulphide will be got.

Place a little in a porcelain crucible and heat strongly. Note the formation of an orange to yellow mass (orange lead). The white lead loses its carbonic acid and water, and is converted into peroxide of lead.

All these tests serve to distinguish white lead from other pigments.

Having prepared white lead and tested it qualitatively, the student may turn his attention to making a quantitative analysis of it. This he may do as follows :—There are three constituents in white lead which require estimating—viz., lead oxide, carbonic acid, and water.

Lead Oxide.—Weigh 2 grammes of the white lead, dissolve in a little pure dilute nitric acid, then add dilute sulphuric acid and a little alcohol (methylated spirit), allow to stand about three to four hours, then filter, wash the precipitate very well with a mixture of one part methylated spirit and ten of water ; then dry the precipitate. Next transfer as much of the precipitate as possible to a porcelain crucible, and burn the filter paper with the remaining portion of the precipitate on the lid of the crucible ; to the ash which remains add a drop of nitric acid, followed by a drop of sulphuric acid, then heat over a Bunsen burner until all acid fumes are given off, place the lid on the crucible, and heat over the Bunsen burner for a short time, then allow to cool and weigh. From the total weight deduct the weight of the crucible and of the filter ash, when the weight of the lead sulphate will be obtained. If this be multiplied by the factor 0·736 the corresponding weight of lead oxide will be obtained, as in the following example :—

Weight of crucible + filter ash + $PbSO_4$, .	11·451
,, crucible alone, . . .	8·653
	2·798
,, filter paper ash, . . .	·0047
,, lead sulphate, . . .	2·7933

$$2·7933 \times 0·736 = 1·726 \text{ PbO}$$

in 2 grammes of the white lead taken.

$$1·726 \times 50 = 86·32 \text{ per cent. PbO.}$$

Carbonic Acid.—The amount of carbonic acid in white lead is best ascertained by using one or other of the many forms of

apparatus which are made for the purpose. Schrotter's is a very good form (see Fig. 8). The apparatus is weighed, a quantity of the white lead is placed in the lower part, C, and then it is weighed again; this gives the weight of the white lead taken. Now fill the apparatus with nitric acid in B, and sulphuric acid in A, which are required, the nitric acid for attacking the white lead, the sulphuric acid for drying the carbonic acid gas as it passes out through A, and a little water with the lead. When these have all been added, the apparatus is weighed. Now the nitric acid is allowed to run on the white lead; when the latter is all dissolved the apparatus is gently heated, then allowed to cool, and weighed. The loss of weight is the amount of carbonic acid in the white lead, from which the percentage is readily calculated.

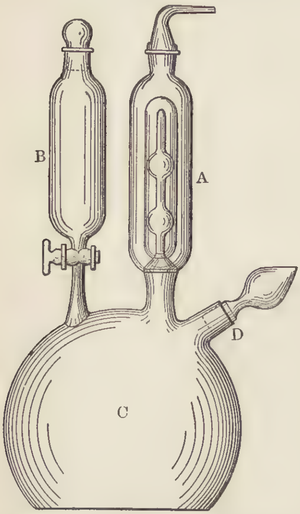


Fig. 8.—Schrotter's carbonic acid apparatus.

The following example will illustrate the mode of working:—

Weight of apparatus + white lead, . .	20·563
,, only, . . .	19·037
White lead taken, . . .	1·506
Weight of apparatus before treatment, . .	50·468
,, after ,, . .	50·297
Loss of carbonic acid, . . .	·171

$$1{\cdot}506 : 0{\cdot}171 :: 100 = 11{\cdot}36.$$

There is then 11·36 per cent. of carbonic acid in the white lead. The amount of water may be taken by difference. The sample of white lead analysed, therefore, contained—

86·32 per cent. of lead oxide, $Pb\,O$.
11·36 ,, carbonic acid, $C\,O_2$.
2·32 ,, water, $H_2\,O$.

The carbonic acid may be calculated to $Pb\,C\,O_3$ by multiplying by 5·9. In the present case there will be—

$$11{\cdot}36 \times 5{\cdot}9 = 68{\cdot}95 \text{ per cent. } Pb\,C\,O_3.$$

The amount of lead oxide corresponding to this is calculated by the difference, thus :—68·95 – 11·36 = 57·59 per cent. of Pb O, leaving 86·32 – 57·59 = 28·73 to combine with water to form hydroxide; the amount of water may be calculated by multiplying by 0·0807. Then in the analysis above we shall have—

$$28{\cdot}73 \times 0{\cdot}0807 = 2{\cdot}32,$$

which shows that in the sample of white lead examined there is neither excess of lead oxide nor of water, but that it is a compound of lead carbonate and lead hydroxide only. In some samples there might be found a slight excess of water, which excess will be present as hygroscopic water ; in other samples there may be a slight excess of lead oxide, which will be shown by there being a deficiency of water present.

MANUFACTURE OF WHITE LEAD.—It may be pointed out here that the Romans were acquainted with a natural white lead, which they called Cerussa, whence modern mineralogists have named it Cerussite. This they used as a pigment, but apparently were not acquainted with any method of making it artificially.

1. *Dutch or Stack Process.*—The principal process for making white lead is the one known as the Dutch or Stack Process which, notwithstanding many attempts to supersede it, still maintains its superiority, although it has many defects. It is carried out in the manner outlined below.

A large shed, varying in size according to circumstances, is built of brickwork ; large works may have several of these side by side. In these sheds are piled layers of the following :—Spent tan, earthenware pots containing dilute acetic acid and a coil of sheet lead, a layer of cast lead plates, called buckles, on the top, and, lastly, a layer of wood boards, in this order until the shed is filled (Fig. 9*a*); then the shed is closed up for some weeks—from eight to ten in summer, ten to thirteen in winter (see Fig. 9*b*).

The tan (replaced at some works by dung) undergoes fermentation, develops heat and evolves carbonic acid. The heat vaporises the acetic acid, which acts upon the metallic or "blue" lead, as it is called, and forms a basic acetate of lead which the carbonic acid transforms into carbonate or white lead. The exact reactions which occur are somewhat uncertain, but may be those represented in the equations.

By the action of moisture and oxygen on the lead there is formed lead hydroxide, thus—

$$1. \quad Pb + H_2O + O = \underset{\text{Lead hydroxide.}}{Pb\,H_2\,O_2}.$$

Then this, being acted on by the acetic acid, forms the normal or neutral acetate and water, thus—

2. $Pb H_2 O_2 + 2 H C_2 H_3 O_2 = Pb 2 C_2 H_3 O_2 + H_2 O.$

The normal acetate now combines with lead hydroxide to form basic lead acetate, thus—

3. $Pb 2 C_2 H_3 O_2 + 2 Pb H_2 O_2 = \underset{\text{Basic lead acetate.}}{Pb 2 C_2 H_3 O_2 \, 2 Pb H_2 O_2}.$

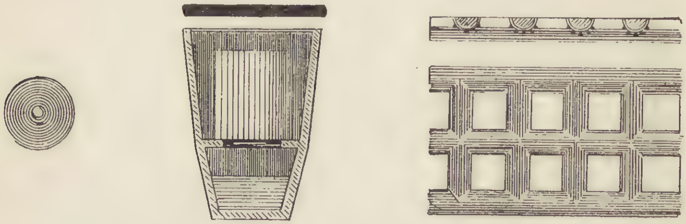


Fig. 9*a*.—White lead pot and lead buckles.

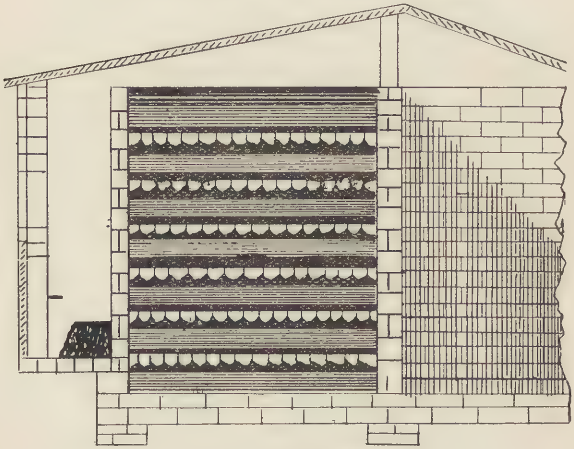


Fig. 9*b*.—White lead stack.

This is now acted upon by the carbonic acid with the formation of white lead and normal acetate, thus—

4. $3 (Pb 2 C_2 H_3 O_2 \; 2 Pb H_2 O_2) + 4 C O_2 =$

$\underset{\text{Normal acetate.}}{3 Pb 2 C_2 H_3 O_2} + \underset{\text{White lead.}}{2 (2 Pb C O_3 \, Pb H_2 O_2)} + 4 H_2 O.$

The normal acetate thus reproduced then forms more tribasic acetate by the reaction shown in equation 3. It is again decomposed by the carbonic acid, as shown in equation 4, so that a continuous cycle of changes is set up, the lead being oxidised to lead hydroxide, and this converted into white lead, the basic carbonate, *pari passu*, with its formation.

As a rule, nearly all the blue lead is converted into white lead, one ton of lead producing one and a quarter ton of white lead, the amount varying from time to time according to the degree of perfection with which the corrosion has proceeded. The great fault of the Dutch process is the great length of time required (8 to 12 weeks), the great amount of capital it takes to construct a stack of lead, and the loss of interest which takes place on the capital while the lead is in process of making. Then there is always a risk, owing to some defect, of producing a useless and imperfectly corroded lead, which has to be sent to the smelting furnace and again reduced to blue lead. Hence it is that inventors have turned their attention to devising other methods of producing white lead which shall be free from the defects of the Dutch process. So far, however, no such method has been discovered.

White lead, as made by the process described above, is a basic carbonate of lead, having the composition—

Lead carbonate, $Pb\,CO_3$, . .	68·95	per cent.
Lead hydroxide, $Pb\,H_2O_2$, . .	31·05	,,
	100·00	,,

or,

Lead monoxide, $Pb\,O$, . .	86·32	per cent.
Carbonic acid, CO_2, . . .	11·36	,,
Water, H_2O, ...	2·32	,,
	100·00	,,

therefore having the formula $2\,Pb\,CO_3, Pb\,H_2O_2$.

The faults of the Dutch or stack process are fairly numerous. The cost of building up a stack is great, and a good deal of capital is locked up for a long time. The stack is unstable and liable to fall, when pots, lead, and tan get mixed up together and are practically wasted. The process cannot be controlled; and while, when everything goes right, the product is excellent, yet occasionally it does not go right, and then the result is bad and the product useless. Attempts have been made by various persons to remedy some of these faults. Walton has devised a plan of building up the stack in a more stable manner, so that it will not fall to pieces while in operation.

German Process.—In this process a chamber is built, in which are a number of shelves; on these are arranged sheets, coils, or plates of lead. When the chamber is filled with the lead the doors are closed, and then currents of steam, acetic acid, and carbonic acid vapours are sent in—in some works alternately, in others simultaneously. In four to five weeks the operation is finished, and then the white lead is taken out of the chamber and prepared for sale in the usual way.

The quality of the product is usually very good, not, perhaps, quite equal to that produced by the Dutch method, but better than that produced by the precipitation processes. It is, however, inclined to be very variable, and the process requires some experience to carry it out in the best possible manner to ensure a good product. It is desirable, as far as possible, to cause the white lead to approximate in composition to the formula $2\,Pb\,C\,O_3, Pb\,H_2\,O_2$, and to do this it is necessary that the gases should be sent into the chamber in the proper proportions. If excess of acetic acid is present, too much acetate of lead is formed, which is not decomposed by the aqueous vapour and the carbonic acid; too much of the latter tends to cause the formation of an excess of lead carbonate, and the white lead loses its covering powers. On the other hand, too much steam will lead to the formation of oxide, especially if the temperature be allowed to get high; the oxide so formed, being of a yellow tint, spoils the colour of the white lead. The same result is brought about by a deficiency of acetic acid. Experience is the only factor which can guide the white-lead maker in adjusting the various gases in the proper proportions.

The following are some analyses of white leads made by this process:—

	1.	2.	3.	4.	5.
Lead monoxide, . .	86·80	86·24	86·03	84·69	83·47
Carbonic acid, . .	11·16	11·68	12·28	14·10	16·15
Water, . . .	2·00	1·61	1·68	0·93	0·25

1. Firsts, of the best quality, good both in colour and body.
2. Seconds, not so good as No. 1, but still very serviceable as a pigment.
3. Thirds is only just usable as a pigment.
4. Is not usable except for very common purposes.
5. Not usable at all, for it contains too much carbonate, and is sent to the smelting furnace.

Kremnitz Process.—This process owes its name to having been worked at Kremnitz in Germany. It is carried on in a chamber built of brick or wood, having a number of shelves on which are placed trays containing a paste made of litharge and either acetic acid or lead acetate, usually in the proportions of 100 lbs. of

litharge to 18 pints of acetic acid, or an equivalent quantity of lead acetate solution. When the chamber is filled, carbonic acid gas is sent into it; this becomes absorbed by the lead oxide present in the paste, the absorption of the gas being facilitated by raking over the paste. The mass originally has a yellowish-grey colour, but as the operation progresses it gradually changes into a white, and when all traces of yellow have disappeared the operation is stopped, and the white lead which is made is first washed with water, then ground, and dried.

Care is taken not to pass the carbonic acid in too long, because this would induce the formation of the normal instead of the basic carbonate, which means poor white lead. When carefully worked good results can be obtained by this process.

The following analysis, presumably of a Kremnitz white lead, is given in Wagner's *Technologie*:—

	Lead oxide,	83·77 per cent.
	Carbonic acid,	15·06 ,,
	Water,	1·01 ,,
or,		
	Lead hydroxide,	8·21 ,,
	Lead carbonate,	91·21 ,,
	Moisture,	0·42 ,,

which shows that this sample did not approach Dutch white lead in composition, but contained more carbonate.

Thenard's Process.—This process, from having been worked on a large scale at Clichy in France, is known as the French process; it is also described in the patent granted to E. Noble in 1808.

The principle of the Thenard process, which is also applicable to many other processes of a similar nature, is that when a solution of normal lead acetate is boiled with litharge, some of the latter is dissolved and a solution of basic lead acetate, known as "Goulard's Extract," "Extract of Saturn," &c., is obtained. The reaction is expressed in the following equation:—

$$\underset{\text{Normal acetate of lead.}}{Pb2C_2H_3O_2} + \underset{\text{Litharge.}}{2PbO} + \underset{\text{Water.}}{2H_2O} = \underset{\text{Basic acetate of lead.}}{Pb2C_2H_3O_22PbH_2O_2}.$$

If a current of carbonic acid is passed through this solution of basic acetate of lead the lead hydroxide it contains is precipitated as a more or less basic carbonate, thus—

$$\underset{\text{Basic acetate of lead.}}{(Pb2C_2H_3O_22PbH_2O_2)} + \underset{\text{Carbonic acid.}}{4CO_2} = \underset{\text{White lead.}}{2(PbCO_3)PbH_2O_2} + \underset{\text{Normal acetate of lead.}}{3Pb2C_2H_3O_2} + 4H_2O.$$

The normal acetate which is thus re-formed can be used again for preparing a fresh solution of basic acetate of lead; of course, while, theoretically, a very little normal acetate is sufficient for the preparation of a large quantity of white lead, and there should be no loss, practically a small quantity of new acetate has to be added from time to time to make up for the little loss which does occur.

In a vessel (1) of convenient size, litharge is dissolved in a solution of lead acetate, the solution being accelerated by heating the solution by means of the steam pipe; from this vessel the liquor runs into another vessel (2) in which all insoluble matter settles out. The clear solution is now run into a trough-shaped vessel (3) into which dips a number of pipes connected with the large main pipe, through which a stream of carbonic acid gas from the generating system flows. This system consists of an oven in which is burnt a mixture of chalk and coke, from which a large quantity of carbonic acid gas is evolved; this gas is washed in the apparatus by passing it through water, after which it passes into the solution of lead in the third vessel, precipitating white lead from it in so doing; the length of time of treating depends upon the quantity and basicity of the lead solution, but usually it takes from twelve to fourteen hours. At the end of this time the current of gas is stopped and the white lead allowed to settle; the clear liquor, which is a solution of the neutral acetate, is run into a fourth vessel, from which it is pumped up by the pump into the first vessel to dissolve more litharge for a fresh operation. The mass of white lead which settles at the bottom of the third vessel is run into a fifth vessel, from whence it passes on to filters to be washed, and then it is finished in the usual way.

The product given by this process is fairly good, but liable to vary in composition from time to time according to the basicity or proportion of lead oxide the lead acetate has dissolved. These are points to which reference will be made in describing other processes.

Cory Process.—The same materials are used in this process as in the last—viz., basic lead acetate and carbonic acid gas, but it differs in the form of apparatus used. The process has been worked on a large scale for a long period. It was first patented in 1838, and the white lead produced by it is favourably spoken of by users. The author believes that the process is still in use.

The plant used consists of a chamber built of brickwork; the bottom is made watertight and sloping towards one end, so that any liquor which may fall upon it drains away into a tank; this

chamber is divided by a number of vertical partitions into compartments; the partitions are so constructed that each alternate one does not quite reach the top, while the others do not quite reach the bottom; the object of this is to make the carbonic acid gas, which is sent into the chamber at one end, take a circuitous course before it passes out at the other end. Above the chamber is a tank, the bottom of which forms the roof of the chamber, which bottom is perforated with a large number of fine holes, so that any liquor which may be run into the tank flows through into the chamber below in a fine stream-like rain. In another tank a solution of basic acetate of lead is prepared in the usual way; this flows into the chamber tank and from thence into the chamber; here it comes into contact with carbonic acid gas which is sent into the chamber, the action between the lead solution and the gas being facilitated by the liquor being in such a finely-divided form.

The lead solution falls to the bottom of the chamber and thence into settling tanks, where the white lead which is formed settles; it is collected, washed, dried, and finished in the usual way, while the solution of neutral acetate of lead, which is also obtained, is used over again.

Many other precipitation processes based on the use of carbonic acid gas have been devised, but they only differ in a few details from the above.

Condy Process.—This process was patented in 1881, and has been worked on a large scale. In this process, acetic acid of 1·045 specific gravity is diluted with about five times its volume of water, and allowed to act on granulated lead until a solution of lead acetate of 1·2 specific gravity is obtained; this solution is evaporated to dryness, when the bibasic lead acetate is obtained. 275 lbs. of bibasic acetate of lead, 112 lbs. of litharge, and 5 gallons of water are ground together into a paste. Instead of preparing the bibasic acetate the neutral acetate may be used; in this case 189 lbs. are ground with 229 lbs. of litharge and 21 lbs. of water for a few hours, and then left for forty-eight hours. In either case there is formed the tribasic acetate of lead. The mass is dissolved in ten times its weight of water, and then for every 112 lbs. of litharge in the mass, 84 lbs. of solid bicarbonate of soda are added; this precipitates the white lead, which is finished in the usual way. A modified process was described in a later patent. One part of acetic acid of specific gravity 1·045 is mixed with twelve and a-half times its weight of water, and the dilute acid so obtained allowed to act upon granulated lead until a solution of specific gravity 1·040 is

obtained; this is mixed with water, and then for every 60 lbs. of acid used in preparing the solution, 30 lbs. of solid bicarbonate of soda are added, and the white lead is precipitated.

The white lead prepared by this process has been favourably spoken of; it has a good colour and covering power. In chemical composition it resembles white lead, but the process appears to be somewhat variable in its results, and, therefore, not commercially practicable.

Other precipitation processes based on the use of alkaline carbonates have been used. The main defect of them is that the product is apt to be crystalline, and then it is short of body.

COMPOSITION AND PROPERTIES.—White lead is sold commercially in two forms. One is a heavy white powder, having a specific gravity of about 6·47 and weighing about 180 lbs. to the cubic foot; it is stated that some processes yield white lead weighing as much as 200 lbs. to the cubic foot. The other form is that of a paste containing about 8 per cent. of linseed oil.

The chemical composition of white lead has already been pointed out. It is a basic carbonate of lead formed by the union of two molecules of lead carbonate, $Pb\,C\,O_3$, with one molecule of lead hydroxide, $Pb\,H_2\,O_2$; this is the composition of the best make of Dutch white lead, which has all the good properties of white lead in the highest degree of perfection.

It is scarcely necessary to point out that as white lead is made by many processes it must necessarily vary in composition; indeed, the white leads yielded by the same process do not always have the same composition, as is evinced by the analyses given here; these have been collected from a variety of sources:—

ANALYSES OF WHITE LEAD.

	1.	2.	3.	4.	5.	6.
Lead monoxide, $Pb\,O$, .	86·35	85·93	83·77	86·5	86·24	84·42
Carbonic acid, $C\,O_2$, .	10·44	11·89	15·06	11·3	11·68	14·45
Water, $H_2\,O$, . .	2·95	2·01	1·01	2·2	1·61	1·36
	99·74	99·83	99·84	100·0	99·53	100·23

from which the composition of the white leads can be calculated to be—

Lead carbonate, $Pb\,C\,O_3$,	63·35	72·15	91·21	68·36	70·87	87·42
Lead hydroxide, $Pb\,H_2\,O_2$,	36·14	27·68	8·21	31·64	28·66	12·33
Moisture, . . .	0·25	...	0·42	...	...	0·48

No. 1. English make. Made by the Dutch process, of very good quality.

No. 2. English make. Made by the Dutch process, of good quality.

No. 3. Krems white. Made by precipitation with carbonic acid gas; this sample is deficient in body although of good colour.

No. 4. German make. Made by the Dutch process, a good white.

No. 5. German make. Made by precipitation with carbonic acid gas, quality fair.

No. 6. German make. Precipitated by carbonic acid gas, of good colour but deficient in body.

The second form in which lead is sold is that of a paste with linseed oil. To make this, the dry white lead, above described, is first mixed in a mixing mill, with about 8 to 9 per cent. of its weight of raw linseed oil; then it is run through a grinding mill several times, to ensure a thorough mixture of the oil and white lead. This form is much favoured by painters, as it is more readily miscible with oil and turps to make into paint.

The following are two analyses of paste white lead :—

Lead hydroxide, $Pb\,H_2\,O_2$, .	65·96	71·14	per cent.
Lead carbonate, $Pb\,C\,O_3$, .	25·19	20·45	,,
Insoluble, . . .	0·70	...	,,
Oil, ...	8·34	8·34	,,

In making this ground white lead only the best raw linseed oil should be used; boiled oil is not admissible, as there would be too much tendency for the lead to become a hard dry mass before it could be used. It is customary to keep ground white lead under water to prevent it drying up too rapidly. Besides its use by painters, this form of white lead is also largely used for other purposes, as a cement for gas piping, &c.

White lead is soluble in dilute nitric acid, and in acetic acid with effervescence, due to the evolution of carbonic acid gas. It is also soluble in boiling dilute hydrochloric acid with effervescence; on cooling the solution, fine transparent needle-shaped crystals of lead chloride separate out. Boiling with sulphuric acid decomposes the white lead, insoluble lead sulphate being formed.

Solutions of white lead in acids give white precipitate of lead sulphate with sulphuric acid; of lead chloride with hydrochloric acid, soluble on boiling in water; and of lead carbonate with sodium carbonate.

Neutral solutions of white lead give a yellow precipitate of

lead chromate with potassium bichromate, and a black precipitate of lead sulphide with sulphuretted hydrogen and solutions of sulphides.

As a pigment white lead possesses all the good qualities desired by a painter—viz., good colour, body or covering power, and permanency. It is distinguished from all other pigments by the ease with which it mixes with oil, and by forming a paint which readily flows from the brush, whereas most pigments, as, for instance, barytes, tend to work what the painter calls slimy or livery, and streaky. White lead does not exhibit this property, but flows freely and evenly from the brush. This feature is generally ascribed to the lead hydroxide in the white lead combining with some of the oil and forming a lead soap, which, dissolving in the rest of the oil used in the preparation of the paint, forms a kind of varnish; this varnish takes up the lead carbonate, to which is due the body or covering power of the pigment. Sometimes this chemical combination between the lead hydroxide and the oil extends to the lead carbonate, and then the white lead loses its opacity and becomes more or less transparent or horny. The conditions most favourable to the production of this change, which is of rare occurrence, are not properly known. This fact of the white lead forming a chemical combination with the oil is well known to colour makers, who have endeavoured, by the addition of basic bodies, to bring about a similar action in the case of other white pigments, such as zinc white and barytes, but so far without any great success.

When exposed to light and air white lead is fairly permanent, and will resist exposure to normal conditions for a great length of time; on the other hand, when exposed to the fumes of sulphuretted hydrogen and other sulphurous gases, white lead turns brown or black through the formation of the black sulphide of lead. The production of this body is more likely to occur in large towns, such as London or Manchester, where large quantities of gas are used for lighting and other purposes, which usually contains some sulphuretted hydrogen or other sulphur compounds. By oxidation this black sulphide can be transformed into the white sulphate of lead; the only agent which can be safely used for this purpose, in restoring paintings which have become discoloured, is peroxide of hydrogen, but the action of this body is very slow and is much interfered with by the oil which is present.

White lead can be mixed with all pigments except those which, like cadmium yellow, ultramarine or king's yellow, contain sulphur; such pigments sooner or later cause the for-

mation of the black sulphide, and thus bring about the discolouration of the pigment or paint.

White lead is frequently adulterated, the pigment most used for this purpose being barytes, because it more nearly approaches white lead in specific gravity, and is, on that account, not so readily detected, whereas the use of whiting or gypsum would soon be detected on account of the lighter weight of the mixture.

This adulteration of white lead is exceedingly common, and is well understood by makers and dealers; in fact, it is the custom for makers to send out several qualities of commercial white distinguished as "genuine," "No. 1," "No. 2," and so on, the degree of adulteration being regulated by the price which is paid for the product. The question whether this is adulteration is a matter of opinion. If by adulteration one means the admixture of cheap products with dear with a view of deceiving purchasers of the latter, then the admixture of barytes with white lead under the conditions named is not adulteration, for the purchaser knows what he is buying, and only pays a fair price for such mixed white leads.

The method of quantitatively examining white leads has already been given.

SULPHATE OF LEAD.

This product is the basis of several white pigments which will be noticed more in detail presently, and, as has been seen, it enters into the composition of chrome yellows, Brunswick greens, &c.

It has the chemical composition shown in the formula $Pb\,SO_4$, and is obtained as a white precipitate when either sulphuric acid or sulphate of soda is added to a solution of acetate of lead or of nitrate of lead.

PREPARATION OF SULPHATE OF LEAD.—Weigh out 10 grammes of acetate of lead, and dissolve it in 200 c.c. of water; then add slowly sulphuric acid until no further precipitate is obtained. Allow this to settle, and pour off the supernatant liquor; wash the precipitate with water, dry, and weigh it. The reaction which takes place is represented in the following equation:—

$$\underset{\text{Lead acetate.}}{Pb\,2\,C_2H_3O_2} + 3\,H_2O + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Lead sulphate.}}{Pb\,SO_4} + \underset{\text{Acetic acid.}}{2\,H\,C_2H_3O_2} + 3\,H_2O,$$

from which it can be calculated that 379 parts of crystallised lead acetate (white sugar of lead) require 98 parts of sulphuric

acid, forming 303 parts of lead sulphate and 120 parts of acetic acid.

It will be noticed that acetic acid is formed as a bye-product in this operation. This may be taken advantage of, when working on the large scale, to form more lead acetate for subsequent precipitation by allowing it to act upon some metallic lead. In the event of doing so, care is taken not to add an excess of the sulphuric acid, but to leave a little unchanged lead acetate in the solution.

Another Method.—Weigh out 10 grammes of lead acetate and 8·5 grammes of Glauber's salt, dissolving each separately in 200 c.c. of water; when both solutions are ready, pour that of the Glauber's salt into the lead acetate; a white precipitate of lead sulphate will be thrown down which may be treated in the way described in the method just noticed.

The reaction which takes place is shown in the following equation—

$$\underset{\text{Lead acetate.}}{Pb2C_2H_3O_2} + 3H_2O + \underset{\substack{\text{Glauber's salt}\\\text{(Sodium sulphate).}}}{Na_2SO_4 + 10H_2O} = \underset{\substack{\text{Lead}\\\text{sulphate.}}}{PbSO_4} + \underset{\substack{\text{Sodium}\\\text{acetate.}}}{2NaC_2H_3O_2} + \underset{\text{Water.}}{13H_2O.}$$

In this case it will be noticed that sodium acetate is obtained as a bye-product which is practically useless. From this equation it will be seen that 379 parts of lead acetate require 320 parts of Glauber's salt (crystallised sodium sulphate) to form 303 parts of lead sulphate and 164 parts of sodium acetate.

The student will do well to make the following experiments with the precipitate of lead sulphate which he obtains :—

1. Boil with a little acetic acid. Note that no change occurs.

2. Boil with a little dilute nitric acid. Note that no change occurs.

3. Boil with an excess of strong hydrochloric acid. Note that, although not easy to dissolve, yet a solution is obtained. Allow one portion to cool; crystals of lead chloride will separate out. To the other portion add a little barium chloride; a white precipitate of barium sulphate will be obtained.

Upon this latter reaction is based the estimation of lead sulphate in pigments.

COMPOSITION AND PROPERTIES.

Lead sulphate has the formula $Pb\,S\,O_4$, and contains

Lead oxide, $Pb\,O$, . .	73·55 per cent.
Sulphuric anhydride, $S\,O_3$, .	26·45 ,,

and of metallic lead 68·31.

It is a white, somewhat crystalline, and very heavy powder, its specific gravity being about 6·3. It is only slightly soluble in water, insoluble in dilute acids and in alcohol, but soluble in solutions of ammoniacal salts, and in strong sulphuric acid; from the latter solution it is precipitated on the addition of water. Boiling concentrated hydrochloric acid dissolves it, and crystals of lead chloride fall down as the solution cools.

As a pigment it is not satisfactory; its crystalline character reduces its body and covering power, causing it often to work streaky or livery under the brush; this defect can be remedied to some extent by grinding it. It is not readily acted upon by sulphuretted hydrogen, and is, therefore, more permanent than white lead under exposure to air. Owing to its solubility being less it is free from the poisonous character of white lead, and, therefore, white pigments containing it are often sold as "non-poisonous white leads." Its colour or hue is a good white, but slightly yellower in tone than white lead, and about equal to barytes.

It is used as a diluent in the manufacture of pale chromes.

SUBLIMED WHITE LEAD.—Under this name has been sold a white pigment prepared by smelting galena, the natural sulphide of lead, in a furnace and blowing air through; the ore oxidises, partly to sulphate and partly to oxide, and is carried away in the form of fume which is collected in a suitable chamber. The original sublimed white lead contained some zinc oxide because it was made from an ore containing some zinc. It was a fairly satisfactory pigment, but liable to vary in quality.

PATENT WHITE LEAD.—This is a sulphate of lead white introduced by Mr. J. B. Hannay, and prepared much in the same way as the sublimed white lead.

FREEMAN'S NON-POISONOUS WHITE LEAD.—This is a mixture of sulphate of lead and zinc white made by grinding the two pigments together for some time. It is a very satisfactory white pigment, is more permanent under exposure to atmospheric influences than white lead, and is equal to white lead in body or covering power and in freedom of working. It is rather heavier than white lead, weighing about 180 to 190 lbs. to the cubic foot. Its specific gravity is 5·95 to 6·00. It is one of the best substitutes for white lead which have been made.

ZINC WHITE.

The important white pigment zinc white is the oxide of the metal, having the chemical formula ZnO.

MANUFACTURE OF ZINC WHITE.—Zinc white is manufactured on the large scale by heating metallic zinc or mixtures of zinc ores and reducing bodies, such as coal or charcoal, in suitable muffle furnaces or retorts; the zinc becomes transformed into vapour and, passing out of the retort, burns and becomes changed into zinc oxide; a strong current of air is caused to pass over the retort mouth in order to ensure the complete combustion of the zinc. This current of air also carries the zinc oxide into large chambers in which the pigment collects.

The product so obtained is a very fine, light powder of a bluish-white tint. Usually the colour is good, but sometimes batches of zinc white have a faint yellow colour, due to impurities in the materials used, such as lead or cadmium, present as oxides, which being yellow in colour impart a faint tint to the zinc white.

PREPARATION OF ZINC WHITE.—Weigh out 5 grammes of zinc sulphate, dissolve in 100 c.c. of water, and add sufficient sodium carbonate dissolved in water to precipitate the zinc as zinc carbonate, $Zn\,C\,O_3$; collect the precipitate on a filter, wash it well with hot water, dry, and transfer as much as possible of the dried carbonate to a porcelain crucible, place this on a tobacco pipe triangle over a Bunsen burner and heat strongly for half an hour.

The carbonate becomes decomposed, carbonic acid is evolved and zinc oxide is left behind, as shown in the equation—

$$Zn\,C\,O_3 = Zn\,O + C\,O_2.$$

Allow the product to cool, and weigh the zinc oxide which is made. Observe that the zinc oxide while hot is of a deep yellow colour, but as it cools down it turns white. This change of colour by heat is characteristic of zinc white.

Try the following experiments with the zinc white so prepared and also with the commercial product:—

1. Treat in a test tube with dilute sulphuric acid. Note that it dissolves without effervescence. This distinguishes zinc white from all other white pigments.

2. Treat in a test tube with acetic acid. Note that it dissolves without effervescence. Hydrochloric acid and nitric acid have the same action. Compare the results with those got with white lead and whiting.

3. To an acid solution add, little by little, ammonia, and note that at first a white flocculent precipitate is obtained, which dissolves on adding an excess of ammonia; to this solution add ammonium sulphide when a white precipitate of zinc sul-

phide is obtained. This reaction distinguishes zinc from all other metals.

4. To an acid solution add a little caustic soda when a white gelatinous precipitate of zinc hydroxide, $Zn H_2 O_2$, is obtained; this is soluble in excess of caustic soda, especially on warming.

COMPOSITION AND PROPERTIES OF ZINC WHITE.—Zinc white, the oxide of zinc, is a compound of the two elements zinc and oxygen in the proportions—

Zinc, Zn, ...	80·25 per cent.
Oxygen, O, ...	19·75 ,,

and has the formula, $Zn O$.

Zinc white is a rather bulky white powder, having a specific gravity of 5·6. In hue it is rather bluish. It is quite insoluble in water, oil, alcohol, and turpentine. It dissolves in dilute sulphuric acid, acetic acid, and many other acids without effervescence, giving colourless solutions. It is also soluble in ammonia and alkaline solutions. It is unchanged by exposure to air and light, and sulphur or sulphur gases have no visible action on it, as the sulphide formed is white like the oxide; as a pigment, therefore, it is quite permanent. It mixes well with all vehicles used in preparing paints. For preparing the stiff paste, which is sometimes sold, it requires about 22 per cent. of linseed oil, a much larger proportion than is required by any other pigment. It mixes well with water, and in this form it is largely used by water colour artists, under the name of Chinese white. It can be mixed with all other pigments without undergoing any change or changing the other pigment. The chief fault of zinc white is its want of body, which is not equal to that of white lead. Its covering power is rather better. This is, no doubt, due to its bulkiness, which is inseparable from the mode of preparation. Many attempts have been made to produce a dense zinc white. The plan most commonly in use is to grind the pigment for some time under edge runners so as to break down, so to speak, the voluminous character of the pigment, and make it more powdery, in which form it has greater covering power. Another proposed plan is to heat the zinc white to a red heat, and then drop it into cold water; the sudden cooling effects the breaking up of the particles of zinc white, but this method is not so effective as the grinding process, and is rather more troublesome to carry out. Its cost, want of body, and want of freedom in working under the brush, have limited the use of zinc white much below that justified by its permanent qualities.

ANALYSIS OF ZINC WHITE.—Zinc white, being a rather costly pigment, is very liable to adulteration with other white pigment, such as china clay, barytes, whiting, terra alba, &c.

Zinc white should be completely soluble in dilute sulphuric acid without effervescence, a property possessed by no other white pigment.

Effervescence indicates an addition of white lead, whiting, or magnesite. Most other adulterants are left as an insoluble residue. The solution in acids is quite colourless. On adding ammonia, a white precipitate is first obtained; but, on adding an excess, this is redissolved; any lead, if present, is left as an insoluble residue. On adding ammonium sulphide to the ammoniacal solution, a white precipitate of zinc sulphide will be obtained; this precipitate should be quite white, or at most have a faint yellow tint, due to its containing traces of the yellow ammonium sulphide; any other colour would indicate impurities. This precipitate should be filtered off, and to the filtrate a solution of ammonium oxalate be added; no precipitate should be obtained; if there is any it indicates the addition either of calcium carbonate in the form of whiting (which is also indicated by effervescence with acids), or of calcium sulphate. If to the solution or filtrate from the ammonium oxalate sodium phosphate be added, the formation of a white precipitate indicates the addition of magnesium.

If a preliminary test with dilute sulphuric acid shows that adulterants are present, it will be best to treat the insoluble residue with hydrochloric acid and then allow the solution to cool; if crystals form, then lead is present, and has been added either in the form of white lead or lead sulphate, the character of the results obtained will indicate which. In the solution, zinc, calcium, and magnesium may be looked for, as described above. If an insoluble residue is left it may contain barytes, china clay, or gypsum, which substances may be tested for in the way described under their respective heads.

The quantity of zinc oxide in a pigment can be thus ascertained. Weigh out about 1 gramme of the pigment, dissolve it in hydrochloric acid, and to the solution add first ammonia in excess, then ammonium sulphide in slight excess; the mixture is placed on one side for a few hours, and then filtered; the precipitate of zinc sulphide is well washed, dried, placed in a porcelain crucible, and ignited at a bright red heat, taking care that plenty of air reaches the material in the crucible; by this means the sulphide is converted into oxide. When the reaction

is considered to be complete, the crucible and its contents are allowed to cool and, when cold, are weighed; the weight of zinc oxide found gives at once the weight of zinc white in the pigment.

ZINC SULPHIDE.

Zinc sulphide is a white pigment composed of the two elements, zinc and sulphur, and has the chemical formula ZnS. It is the only white insoluble sulphide.

PREPARATION OF ZINC SULPHIDE.—Weigh out 5 grammes of zinc sulphate, dissolve in 100 c.c. of water, then add ammonium sulphide in sufficient quantity to precipitate all the zinc. The reaction which takes place is shown in the equation—

$$\underset{\text{Zinc sulphate.}}{ZnSO_4} + \underset{\text{Ammonium sulphide.}}{(NH_4)_2S} = \underset{\text{Zinc sulphide.}}{ZnS} + \underset{\text{Ammonium sulphate.}}{(NH_4)_2SO_4}.$$

The precipitate obtained is allowed to settle. It is then washed by decantation and dried, when it is obtained as a white powder.

The student should make the following tests with it:—

1st. Treat with hydrochloric acid. Note that it dissolves to a clear solution, sulphuretted hydrogen (distinguished by its odour) being evolved.

This distinguishes zinc sulphides from other whites.

2nd. Treat with ammonia. Note that it remains undissolved.

3rd. Add to the acid solution sufficient ammonia to neutralise the solution, and then a little ammonium sulphide. Note that the ammonia first produces a precipitate, which it re-dissolves, and that the last reagent gives a white precipitate. This is very characteristic of zinc.

Zinc sulphide is not much used as pigment except for colouring india-rubber; but in combination with barium sulphate and zinc oxide it enters into the composition of the white pigment known variously as Orr's white, Griffith's white, lithophone, the last name being the one by which it will probably be the best known in the future.

When prepared for use as pigment on the large scale, sodium sulphide is used in place of the ammonium sulphide. It is important that it should be of a good white colour, and free from impurities which might have an action on the rubber which it is used to colour. The materials used should be free from lead, iron, or copper, which would lead to the production of black sulphides.

Zinc sulphide when pure consists of—

Zinc, ...	67·01 per cent.
Sulphur, ...	32·99 ,,

LITHOPHONE.

Lithophone was first introduced in 1874 by Mr. J. B. Orr under the name of Charlton white, since which time it has acquired quite a distinct place among white pigments, and has become better known by the name of lithophone or lithopone, although it is known under other names.

It is a combination of zinc sulphide, zinc oxide, and barium sulphide, prepared by double precipitation of zinc and barium compounds and furnacing the precipitate.

PREPARATION OF LITHOPHONE.—Weigh out $8\frac{1}{2}$ grammes of zinc sulphate and 6 grammes of barium sulphide; dissolve each separately in 200 c.c. of water, and, when dissolved, mix the two solutions. A combined precipitate of barium sulphate and zinc sulphide will be obtained, as indicated in the equation—

$$\underset{\text{Zinc sulphate.}}{Zn\,S\,O_4} + \underset{\text{Barium sulphide.}}{Ba\,S} = \underset{\text{Precipitate.}}{Ba\,S\,O_4\,Zn\,S.}$$

Collect this precipitate, wash it well with water, then dry it; place the white powder in a crucible, cover it with a lid and heat to a red heat for half an hour, then allow to cool, and grind it in a mortar to a fine powder, when it will be finished. The heating changes some of the sulphide to oxide of zinc.

Another Method.—A more convenient method for the student of preparing lithophone is to weigh out 5·7 grammes of zinc sulphate, 5·9 grammes of barium chloride, and 15 grammes of sodium sulphide; dissolve each separately in 100 c.c. of water, then pour the barium chloride solution into the zinc sulphate solution, and, lastly, the sodium sulphate solution into the mixture.

A combined precipitate of zinc sulphide and barium sulphate is thereby obtained. The reactions which occur are shown in the equations—

$$Zn\,S\,O_4 + Ba\,Cl_2 = Ba\,S\,O_4 + Zn\,Cl_2.$$

Zinc sulphate reacts with barium chloride to form barium sulphate, which precipitates out, and zinc chloride, which remains in solution.

$$Zn\,Cl_2 + Na_2\,S = Zn\,S + 2\,Na\,Cl.$$

Zinc chloride reacts with sodium sulphide to form zinc sulphide, which precipitates out, and sodium chloride, which remains in solution and is washed away.

The precipitate should be collected on a filter, well washed with water, dried, heated in a crucible (as described before), and then weighed.

This precipitate may then be subjected to the following tests :—

1. Treat with hydrochloric acid. Note that an odour of sulphuretted hydrogen is evolved, indicating the presence of zinc sulphide. Some remains insoluble. Filter this off, and add to the filtrate ammonia and ammonium sulphide; the white precipitate of zinc sulphide will be obtained. The barium sulphate left insoluble on the filter can be identified by its insolubility in acids, and the green tinge it gives to the Bunsen flame.

A quantitative analysis may be made in the following manner:— Two grammes are weighed out into a beaker and treated with hydrochloric acid; after all action has ceased, the mixture is diluted with water and filtered, the residue on the filter paper being washed with water, dried, burnt in a crucible, and again washed. This gives the weight of barium sulphate in the sample.

The filtrate from this residue is neutralised by adding first ammonia, then ammonium sulphide, the mixture being placed on one side for a few hours; it is then filtered, and the precipitate of zinc sulphide filtered off, dried, and burnt in a crucible, the zinc oxide which is obtained being weighed. This gives the total amount of zinc in the sample, present both as oxide and sulphide.

The next proceeding is to determine the amount of zinc sulphide in the sample; for this purpose weigh out 2 grammes and treat with 25 c.c. of strong nitric acid, heating the mixture to the boil. This converts the zinc sulphide into the zinc sulphate. Dilute the mixture with water, filter from the insoluble barium sulphate, add to the filtrate barium chloride, filter off the precipitate of barium sulphate which is obtained, wash it well with warm water, dry, burn, and weigh it. By multiplying the weight so found by 0·416 ($Ba\,S\,O_4 = Zn\,S$, 233 = 97), the corresponding weight of $Zn\,S$ will be obtained.

By multiplying the weight so found by 0·347 ($Ba\,S\,O_4 = Zn\,O$, 233 = 81), the corresponding weight of zinc oxide will be obtained. This is to be deducted from the total zinc oxide found to ascertain the quantity of zinc present as oxide in the sample.

Any moisture in the sample may be determined by weighing

2 grammes in a crucible, heating for a few minutes over the Bunsen burner, and weighing again. The loss of weight represents the amount of moisture present.

The following data, which have been obtained by the author in an actual analysis of a sample of lithophone, will illustrate the above scheme and show the method of calculating :—

1st. For *Barium sulphate.* 2 grammes of sample taken.

Weight of $Ba\,S\,O_4$ + crucible + filter ash, .	14·160
,, crucible, ...	12·540
,, $Ba\,S\,O_4$ and filter ash, . .	1·620
,, filter ash, ...	·0047
Weight of barium sulphate, . .	1·6153

2 : 100 : : 1·6153 : 80·76.

80·76 per cent. $Ba\,S\,O_4$.

2nd. For *Total zinc calculated as oxide.* 2 grammes of sample taken.

Weight of $Zn\,O$ + crucible + filter ash, .	12·855
,, crucible, ...	12·54
,, $Zn\,O$ and filter ash, . . .	·315
,, filter ash, ...	·0047
Weight of zinc oxide, . . .	·3103

2 : 108 : : ·3103 : 15·51.

15·51 per cent. of $Zn\,O$.

3rd. For *Zinc sulphide.* 2 grammes of sample taken.

Weight of $Ba\,S\,O_4$ + crucible + filter ash, .	13·289
,, crucible, ...	12·540
,, $Ba\,S\,O_4$ and filter ash, . .	·749
,, filter ash, ...	·0047
Weight of barium sulphate, . .	·7443

·7443 × ·416 = ·3096.

2 : 100 : : ·3096 : 15·48.

15·48 per cent. zinc sulphide.

·7443 × ·347 = 12·91.

12·91 per cent. of $Zn\,O$ as $Zn\,S$ in the sample.

Total zinc as oxide, ...	15·51
Zinc oxide equal to the zinc sulphide, .	12·91
Zinc oxide in sample, . . .	2·60

4th. For *Water*. 2 grammes of sample taken.

Crucible white, before, . . .	22·540
,, ,, after, . . .	22·517
	·023

2 : 100 : : ·023 : 1·15.

1·15 per cent. water.

Adding up these results we shall have the composition of the white as—

Zinc sulphide, $Zn\,S$, . . .	15·48	per cent.
Zinc oxide, $Zn\,O$, . . .	2·60	,,
Barium sulphate, $Ba\,S\,O_4$, . .	80·76	,,
Water, H_2O, ...	1·15	,,
	99·99	,,

MANUFACTURE OF LITHOPHONE.—Orr manufactured the original pigment in the following manner :—

Barium sulphide was prepared by fusing finely-ground barytes with charcoal, and lixiviating the fused mass with water to separate out the sulphide so made. This was then divided into two equal portions; to one was added an equivalent quantity of a solution of zinc chloride, when a precipitate of zinc sulphide is obtained according to the equation—

$$Ba\,S + Zn\,Cl_2 = Zn\,S + Ba\,Cl_2.$$

To the mixture was now added the remainder of the barium sulphide and an equivalent quantity of zinc sulphate, when a combined precipitate of zinc sulphide and barium sulphate is obtained according to the equation—

$$Ba\,S + Zn\,S\,O_4 = Zn\,S + Ba\,S\,O_4.$$

The whole precipitate, consisting of two equivalents of zinc sulphide to one of barium sulphate, is collected on a filter, well washed with water, dried, and calcined in a furnace to convert some of the zinc sulphide into zinc oxide.

Made in this way Orr's white or lithophone has the composition :—

Barium sulphate, ...	69·9	per cent.
Zinc sulphide, ...	14·7	,,
Zinc oxide, ...	13·3	,,
Water, ...	2·1	,,

Lithophones are now made which contain a large proportion of barium sulphate; to obtain these a solution of barium sulphide is first precipitated with zinc chloride; then to the mixture is added barium chloride and sufficient sodium sulphate to throw down all the barium as sulphate, the pigment being finished as before. Some of these lower grades of lithophone contain 80 to 85 per cent. of barium sulphate.

Sometimes the strontium sulphide is used in place of the barium sulphide when the pigment will contain strontium sulphate. These strontium pigments are not so easy to prepare as the barium pigments, but they are equal in quality.

The following proportions may be used :—For best grade of lithophone 308 lbs. of solid zinc chloride in 340 gallons of water, 383 lbs. of barium sulphide in 340 gallons of water, then 730 lbs. of Glauber's salt in 600 gallons of water. For common grade use the above and, in addition, 595 lbs. of barium chloride in 450 gallons of water, and 1460 lbs. of Glauber's salt in 1136 gallons of water.

The lithophone whites are excellent pigments; when well made they are of a good white colour, are fully equal, and in many cases are superior, to white lead in covering power, while it possesses the advantage of not being discoloured with sulphur compounds. It is non-poisonous. It mixes well with almost all other pigments, except lead and copper pigments, which are liable to be discoloured from the formation of the sulphides. Being lighter in gravity than white lead it does not settle so freely when mixed with oil into paints.

BARYTES.

Barytes is the natural mineral of the same name prepared for use as a pigment by grinding and levigating with water, accompanied by treatment with acid and drying. This mineral occurs more or less pure in many parts of the world and passes under a variety of names; cawk is the one used by the Derbyshire lead miners, lead bloom in some places, while heavy spar is a common name given on account of its great weight. In the British Isles it is found in Cornwall, Derbyshire, Cumberland, Lancashire, Devonshire, Wales, Ireland, Scotland, and elsewhere. The best grades are white and crystalline; some have a creamy tint due to the presence of oxide of iron. A sample of Derbyshire barytes analysed by the author had the composition—

Barium sulphate, $Ba\,S\,O_4$, . .	98·56	per cent.
Ferric oxide, $Fe_2\,O_3$, . . .	·83	,,
Calcium sulphate, $Ca\,S\,O_4$, . .	·50	,,
Magnesia, $Mg\,O$, . . .	·01	,,

with a specific gravity of 5·02.

In preparing barytes on the large scale, the grinding should be well done, and in order to remove the creamy tint the mineral should be treated with a mixture of hydrochloric and sulphuric acids and then well washed afterwards, finally dried.

COMPOSITION AND PROPERTIES OF BARYTES.—Barytes is a fine and rather heavy white powder, having a specific gravity of 4·5 to 4·75. It has a more or less crystalline structure, which causes it to have a slight gritty feel, no matter how fine it may be ground. It is quite insoluble in all acids and alkalies, a property (or, rather, properties) which distinguishes it from other white pigments. It is quite unaffected by any injurious influences such as affect white lead, and, therefore, as a pigment it is the most permanent white known; for this reason it has been called, and sold as, constant white, permanent white, &c.

In body or covering power it is much inferior to either white lead or lithophone, but it is better than zinc white. It mixes very well with oil, of which it takes about 7 per cent. to grind into a stiff paste; as an oil paint it is satisfactory in use, but for water colours it is not so good, seeming to lose some of its body on mixing with water.

It is largely used for mixing with other pigments, especially with white lead, many commercial samples of which contain from 20 to 25 per cent. of barytes; its presence in such is easily detected by its insolubility in acids and its tinging the Bunsen flame green.

ANALYSIS OF BARYTES.—There being no cheaper pigment, barytes is never adulterated, but it is used as an adulterant in other pigments. It is distinguished by its high specific gravity, being heavier than any other white pigment, except white lead, and by its insolubility in acids, which distinguishes it from all other white pigments except china clay. Barytes can be detected by moistening a little with hydrochloric acid, and holding it on a platinum wire in the lower part of a Bunsen flame when, if barytes is present, the latter will become tinted with a pale yellow-green colour. It is not always easy to see this colour, as sometimes it only comes in flashes, while at others it is more persistent; much depends upon the amount of acid used. With a little care the presence of barytes in any pigment may be detected by this test.

BLANC FIXE.

This pigment is also barium sulphate, but prepared artificially.

PREPARATION OF BLANC FIXE.—Weigh out 10 grammes of barium chloride and dissolve in 150 c.c. of cold water, then add, slowly, sufficient dilute sulphuric acid to precipitate the whole of the barium; allow the white precipitate of barium sulphate which is obtained to settle, pour off the clear supernatant liquor, pour on the residue some clean water, stir well, pour the mass through a filter, and then dry the blanc fixe which collects on the filter, and weigh it.

The reaction which takes place between the barium chloride and the sulphuric acid is shown in the following equation :—

$BaCl_2$	+	H_2SO_4	=	$BaSO_4$	+	$2HCl$
Barium chloride.		Sulphuric acid.		Barium sulphate (blanc fixe).		Hydrochloric acid.

from which it is seen that 208 parts by weight of barium chloride require 98 parts of sulphuric acid to precipitate 233 parts of blanc fixe, while 73 parts of hydrochloric acid are formed.

Blanc fixe is also obtained whenever a soluble sulphate—Glauber's salt, alum, sulphate of alumina, chrome alum—is added to a solution of a soluble barium salt. This property is taken advantage of in the preparation of many substances, so that it follows that blanc fixe (barium sulphate) is a bye-product obtained in other chemical operations.

The student should try the effect of heat, the action of boiling caustic soda, of strong hydrochloric acid on the precipitate which he obtains, and he will probably find that none of these have any action on it; in fact, barium sulphate is one of the most refractory compounds known. One test for barium sulphate is the flame test. If a little be moistened with hydrochloric acid and held on a piece of platinum wire at the base of a Bunsen flame, the latter becomes tinged with a yellowish-green colour that often comes out as flashes, and is as often as not rather difficult to obtain.

Blanc fixe is an excellent pigment, for it has good covering powers, and, what is better, is quite permanent in every respect, a property in which it is second to none.

Another barium mineral is witherite, the carbonate, $BaCO_3$, which is sometimes ground and sold as barytes, or at other times used in making blanc fixe by dissolving it in hydrochloric acid and precipitating with sulphuric acid.

GYPSUM.

The mineral gypsum is the natural hydrated sulphate of calcium, and is fairly abundant in a variety of forms in various localities. When in clear transparent masses which can be easily cleaved into thin plates it is called selenite; when in long, fibrous, silky masses it is called satin spar; when in shiny opaque masses, alabaster. In colour it varies from pure white to reddish masses, sometimes streaky. It is met with at Chellaston, near Derby, Aston-on-Trent, Newark-on-Trent, Fauld, and at other places. The pieces which are in variegated colours are used for ornamental purposes. The white lumps are ground up and used for a pigment which is called terra alba, mineral white. Gypsum is easily ground up, for it is a soft mineral, easily scratched. Its specific gravity is 2·28 to 2·33.

Its chemical composition is—

Calcium oxide, CaO, . . .	32·6 per cent.
Sulphuric anhydride, SO_3, . .	46·5 ,,
Water, H_2O, ...	20·9 ,,

corresponding to the formula $CaSO_4\,2H_2O$.

PROPERTIES OF GYPSUM.—The colour of gypsum is generally very good, and in tone is a bluish-white, rather bluer than barytes, but not so blue as white lead; occasionally samples may have a yellow tint, which is due to the presence of oxide of iron, which, however, can be eliminated by treatment with acids, as in the case of bleaching barytes. It is much lighter than either white lead or barytes, but is rather heavier than china clay or zinc white. Its body is not as good as that of white lead, but it is at least equal to barytes in that respect. It mixes well with water, but is rather transparent when mixed with oil. Being neutral in its properties, it can be mixed with all other pigments without affecting them, or being affected by them in any way. On exposure to light and air it is unaffected, being one of the most permanent pigments known. It is used very largely by paper stainers and makers of paper hangings, who prefer it to barytes on account of its having more body when used for that class of work. It is used in the finishing of cotton goods, in paper-making, and for a variety of other purposes where a cheap white pigment is required.

Gypsum is slightly soluble in water, about 1 part in 500; this solution will give a precipitate of calcium oxalate on addition of ammonium oxalate and a precipitate of barium sulphate on addition of barium chloride. It is more soluble in hydrochloric

acid; long boiling with dilute hydrochloric acid will dissolve it without effervescence, and the solution will show the presence of both calcium and sulphuric acid on the application of the usual tests for those bodies. Gypsum is also soluble in solutions of ammonium salts.

At a temperature of about 300° F. gypsum loses its water of crystallisation and forms a white powder, which has the property of combining with water and setting into a hard mass; this property is a very important one, the manufacture of the white powder being carried on on a large scale, and the product sold under the name of plaster of Paris for various ornamental and useful purposes.

A chemical analysis is rarely required, and it can be made in the usual way, oxide of iron, silica, barytes, and whiting being the substances most likely to be added or present in a sample of gypsum.

Generally the gypsum offered commercially is nearly pure, containing about 78·5 per cent. of calcium sulphate, the rest being water of crystallisation.

SATIN WHITE.

This is an artificial white pigment consisting of a mixture of calcium sulphate and aluminium hydroxide, much used in the paper and cotton cloth finishing trades.

PREPARATION OF SATIN WHITE.—Weigh out 8 grammes of quicklime, and, after shaking with water, make into a thin cream by adding more water. Weigh out 17 grammes of alumina sulphate and dissolve in 25 c.c. of water. Mix the two preparations and heat to the boil, then allow to settle, decant the clear liquor, wash the residue of satin white which is obtained with water, filter, dry, and weigh it. The reaction which takes place between the two bodies used is given in the following equation:—

$$\underset{\text{Slaked lime.}}{3\,Ca\,H_2O_2} + \underset{\text{Alumina sulphate.}}{Al_2\,3\,S\,O_4} = \underset{\text{Alumina hydrate.}}{Al_2\,H_6\,O_6} + \underset{\text{Calcium sulphate (satin white).}}{3\,Ca\,S\,O_4}$$

which shows that 222 parts by weight of slaked lime (equal to 168 parts of quicklime), react with 343 parts of alumina sulphate to form 390 parts of satin white, for it happens in this case that the two substances alumina hydrate and calcium sulphate are both insoluble in water, and are simultaneously precipitated out to form satin white.

If, therefore, the lime and alumina sulphate are correctly proportioned to one another, no bye-product is formed, as is the

case with the blanc fixe above, and most, if not all, of the previous examples of preparing pigments by precipitation.

The precipitate of satin white so obtained may be examined as follows :—Boil a portion with a little strong hydrochloric acid, filter the solution, and divide the filtrate into two portions; to one add a little ammonia, when a white gelatinous precipitate of alumina hydrate is obtained. This proves the presence of alumina in the satin white. To the other portion add a solution of barium chloride, when a white precipitate of barium sulphate is obtained, which shows the presence of a sulphate. If the precipitate of alumina obtained by the ammonia be filtered off and ammonium oxalate added to the filtrate, a white precipitate of calcium oxalate will be obtained, showing the presence of lime in the satin white. If a portion be moistened with hydrochloric acid and held on platinum wire in the Bunsen flame, a reddish tinge is imparted to the latter, which again is indicative of the presence of lime (calcium oxide).

The proportion of alumina hydrate and calcium sulphate may be ascertained in the following manner :—Two grammes of the satin white are weighed out and boiled with 20 c.c. of water and 20 c.c. of hydrochloric acid for a short time. This dissolves out all the alumina hydrate and part of the calcium sulphate, together with any excess of free lime that may be in the sample. Filter the mass from any undissolved calcium sulphate, wash the residue with water, and add the first washings to the filtrate. The residue is dried, burnt in a weighed crucible, and weighed. This is taken as calcium sulphate. To the filtrate is added ammonia; the precipitate of alumina hydrate which is obtained is filtered off, washed, dried, burnt in a crucible, and weighed as alumina ($Al_2 O_3$). The weight of hydrate ($Al_2 H_6 O_6$) is calculated from this by multiplying by $1{\cdot}524 = Al_2 H_6 O_6 \div Al_2 O_3 = 157 \div 103$.

The filtrate from the alumina is divided into two equal portions. To one is added ammonium oxalate, which will throw down a precipitate of calcium oxalate; the mixture is allowed to stand for some time to allow all the lime to precipitate, then it is filtered off, dried, burnt in a crucible, and the residue of calcium carbonate ($Ca C O_3$) weighed. From this we shall get the amount of free lime present, as will be seen presently.

The second portion of the alumina filtrate is acidulated with hydrochloric acid and heated to the boil and barium chloride added, which throws down a white precipitate of barium sulphate. This is filtered off, well washed with water, dried, burnt in a crucible, and weighed.

From the weight of barium sulphate so found the weight of calcium sulphate can be calculated by multiplying by 0·583 ($Ba\,S\,O_4 = Ca\,S\,O_4$; 233 = 136). The weight so calculated is to be added to that found as insoluble in the acid. The barium sulphate is also to be calculated to the equivalent quantity of calcium carbonate by multiplying by 0·429 ($Ba\,S\,O_4 = Ca\,C\,O_3$; 233 = 100). The difference between this weight and that of the calcium carbonate found by means of ammonium oxalate represents the amount of free lime.

The student will thus have determined the amounts of alumina hydrate, calcium sulphate, and calcium carbonate in the sample.

The following figures were obtained by the writer in an analysis of a sample of satin white :—

1st. *Moisture.* 5 grammes of sample taken.

Crucible + satin white, before, . . .	9·899
,, ,, after, . . .	9·372
	0·527

5 : 100 :: 0·527 : 10·54.

10·54 per cent. water.

2nd. *Alumina.* 2 grammes of sample taken.

Crucible + alumina + filter ash, . .	6·2310
Crucible, ...	5·6700
Alumina and filter ash, ...	·5530
Filter ash, ...	·0027
$Al_2\,O_3$ found, . . .	·5503

2 : 100 :: ·5503 : 27·51.

27·51 per cent. alumina, $Al_2\,O_3$.

3rd. *Calcium sulphate (insoluble).*

Crucible + $Ca\,S\,O_4$ + filter ash, . .	6·4550
Crucible, ...	5·9220
Calcium sulphate and filter ash, . .	·5330
Filter ash, ...	·0027
$Ca\,S\,O_4$ found, . . .	·5303

2 : 100 :: ·5303 : 26·51.

26·51 per cent. $Ca\,S\,O_4$ (insoluble).

4th. *Calcium sulphate dissolved.* The filtrate from the alumina precipitate was made up to 100 c.c. and 50 c.c., equal to 1 gramme of the satin white taken.

Crucible + $Ba\,S\,O_4$ + filter ash, . .	6·3740
Crucible, ...	5·9220
Barium sulphate and filter ash, . .	·4520
Filter ash, ...	·0027
$Ba\,S\,O_4$ found, . . .	·4493

233 : 136 :: ·4493 : 262.

1 : 100 :: ·2623 : 26·23.

26·23 per cent. $Ca\,S\,O_4$ (dissolved).

5th. *Total calcium carbonate.* 50 c.c. of the filtrate from the alumina precipitate taken and ammonium oxalate added.

Crucible + $Ca\,C\,O_3$ + filter ash, . .	6·2540
Crucible, ...	5·9680
Calcium carbonate and filter ash, . .	·2860
Filter ash, ...	·0027
$Ca\,C\,O_3$ found, . . .	·2843

$Ba\,S\,O_4 = Ca\,C\,O_3 : 233 = 100.$

233 : 100 :: ·4493 : ·1928.

Total $Ca\,C\,O_3$ found, ...	·2843
$Ca\,S\,O_4$ as $Ca\,C\,O_3$, ...	·1938
Free $Ca\,C\,O_3$, . . .	·0915

1 : ·0915 :: 100 : 9·15.

9·15 per cent. free $Ca\,C\,O_3$.

Summarising these results, we have as the composition of satin white :—

Water, H_2O, ...	10·54	per cent.
Alumina, Al_2O_3, . . .	27·51	,,
Calcium sulphate, $Ca\,S\,O_4$, . .	52·74	,,
Calcium carbonate, $Ca\,C\,O_3$, . .	9·15	,,
	99·94	

MANUFACTURE OF SATIN WHITE.—The manufacture of satin white on the large scale is on the same lines as in the laboratory experiment given above. There may be used 56 lbs. of quicklime and 114 lbs. of alumina sulphate. The lime should be slaked in a wooden vat with a fair proportion of water, and sieved from that into a larger vat. The sulphate of alumina can be dissolved in a separate vat, and, when dissolved, run into the lime, and the whole boiled with steam for a short time, then finished as are other pigments made in the same way. Both materials should be of good quality, if a good grade of satin white be wanted.

PROPERTIES OF SATIN WHITE.—Satin white has a fine white colour; it is excellent as a water-colour pigment, but works only moderately well in oil, being somewhat transparent; it is, however, better than gypsum. It is quite permanent, and mixes well with all other colours.

It is distinguishable from gypsum by being rather more soluble in acids, and giving a precipitate of alumina on the addition of ammonia to solutions of it, as is indicated in the tests given above.

WHITENING OR WHITING.

In Sussex and Kent there are immense beds of a soft, white rock-chalk. These are quarried in many places, especially where the quality is good, and ground in suitable mills, then levigated to free it from grit, particles of flint, silica, &c., after which it is dried. The white pigment is known under a variety of names, the most common of which is "whiting" or "whitening," from its use in the distempering of walls, ceilings, &c. The best and finest grades are often called Paris white, while Spanish white is an old name for the substance.

PREPARATION OF CALCIUM CARBONATE.—Whiting consists almost entirely of calcium carbonate, a compound of calcium oxide (lime), $Ca\,O$, and carbonic acid, $C\,O_2$. It contains 40 per cent. of calcium, 12 per cent. of carbon, and 48 per cent. of oxygen, corresponding to the formula $Ca\,C\,O_3$. It may be prepared on the small scale as follows:—Weigh out 5 grammes of calcium chloride, dissolve in 100 c.c. of water, and add slowly a solution of ammonium carbonate, or of sodium carbonate, till no further precipitate is obtained. Filter off the white precipitate of calcium carbonate which is got, wash well with water, then dry and weigh the precipitate.

Test the calcium carbonate so obtained in the following manner:—

1. Treat a small portion with hydrochloric acid in a test tube. Observe that it dissolves with effervescence, and compare this result with that obtained with white lead.

2. Treat in a similar manner with sulphuric acid, and observe that no solution is obtained.

3. To the hydrochloric acid solution add, first, ammonia, when no precipitate will be obtained; then add a little ammonium oxalate, when a white precipitate of calcium oxalate will be obtained.

4. Heat a portion of the calcium carbonate strongly over the Bunsen burner in a porcelain crucible; then treat the residue

with water. Notice the heat evolved. The heat used has changed the calcium carbonate into calcium oxide (quicklime), while carbonic acid is evolved.

5. Dip a piece of platinum wire into the hydrochloric acid solution, and hold it in the Bunsen flame. Notice the red colouration imparted to the flame.

MANUFACTURE OF WHITING.—For use as a pigment the chalk is quarried, ground under water in edge-runner mills to a coarse powder, then passed to flatstone mills, where it is ground very fine; from which mills it is run into tanks, in which the coarser and heavier grit and sand settles, while the finer chalk passes on to other tanks, in which it settles. When the settling tanks or pits are full, the chalk or whiting is dug out and dried. It is first taken to a hot room, on the floor of which it is thrown in heaps. Under the floor are a number of flues connected with a furnace fed from the outside of the chamber; sometimes the flues do not pass in the same manner as in the drying room used in making barytes. In this room it remains about twelve hours, when the great bulk of the water it contains will have evaporated away. The partially dry mass is now cut into masses of a cubical shape, and taken to a large drying room constructed similarly to those used for barytes and other pigments. In this hot chamber it is placed on iron racks, and kept there until it is thoroughly dry, which will take from twenty-four to forty-eight hours, according to the degree of dryness of the whiting, and to the temperature of the drying stove; the drying is also facilitated if a current of air is sent through the drying room during the process, as is done in some works. The temperature of the drying stove should not be too high, and in arranging the whiting on the racks it is advisable not to place it in any position where it is liable to be subjected to extreme heat. After being dried, the whiting is ground in a flatstone mill before it is sent out for use.

Paris white is a finer quality of whiting, prepared from chalk in the same way, but the grinding is more thoroughly done. Spanish white is an old name given to Paris white sold in a cylindrical form prepared by moulding the wet material into that form, and allowing it to dry in the open air.

COMPOSITION AND PROPERTIES OF WHITING.—Whiting is a dull white powder of an amorphous character and soft to the feel. It is moderately heavy, the specific gravity being about 2·5 to 2·8. It consists chiefly of calcium carbonate, but it may also contain traces of silica, water, &c. The following

analysis of an ordinary commercial sample will show the average composition of whiting :—

Calcium carbonate, $Ca\,C\,O_3$, .	.	94·795 per cent.
Silica, $Si\,O_2$, .	. . .	3·030 „
Water, H_2O, .	. . .	2·175 „

It is quite insoluble in pure water, but in water containing carbonic acid gas in solution it is soluble. It is also soluble in acids, such as acetic, hydrochloric, nitric, &c., with effervescence, due to the evolution of carbonic acid gas. Sulphuric acid decomposes it with effervescence, carbonic acid being evolved and insoluble calcium sulphate formed. There are but few white pigments which are soluble in acids with effervescence; white lead and whiting are the most common, while the carbonates of barium, strontium, and magnesium are occasionally met with.

Heat decomposes it with the evolution of carbonic acid gas, $C\,O_2$, and the separation of calcium oxide, quicklime, $Ca\,O$. This property is taken advantage of in preparing lime for making cements, mortars, &c.

As a pigment it is mostly used as body colour in distemper work, colouring walls, ceilings, &c., using water as a vehicle. It is not used as an oil colour, for it is subject to the defect that, when mixed with oil, it loses its white colour and turns a dirty grey; mixed with about 18 per cent. of linseed oil, it forms the useful article known as putty.

It has a tendency to be somewhat alkaline in its properties. In this respect much depends upon the care which has been exercised in drying the whiting during the process of manufacture; over-heating is apt to cause the formation of small quantities of quicklime, which increases the alkaline properties of the whiting. It is not safe, therefore, to mix it with such pigments as Prussian blue, chrome yellow, verdigris, emerald green, &c., which are more or less affected by alkalies. Most other pigments—ultramarine, yellow ochre, oxide reds, &c.—are not affected by whiting in any way.

It is quite permanent when used as a pigment, and is not at all acted on by any of the ordinary atmospheric agents which are often destructive to pigments.

Whiting is distinguished by the following tests:—It is soluble in dilute hydrochloric acid with much effervescence; there may be left undissolved small traces of silica in a gelatinous form, but no considerable amount of white powdery insoluble residue will be found. On adding to this solution ammonium chloride and ammonia, no precipitate of iron or alumina should be obtained, or, at most, a very slight one. On further adding

ammonium sulphide, no precipitate should be obtained. Addition of ammonium oxalate to the same solution throws down a white precipitate of calcium oxalate. The filtrate from this should not give with sodium phosphate more than a mere trace of a precipitate of magnesium phosphate.

The quantity of calcium carbonate or whiting which may have been added to any pigment may be ascertained by throwing it down as calcium oxalate, as described above, and then filtering off this precipitate; it is best to allow it to stand for some time before filtering, so as to give time for the precipitation to become complete. The precipitate is well washed, then dried, placed in a weighed crucible, burned, and weighed in the usual manner. The weight of the residual calcium carbonate gives the weight of the whiting in the sample taken.

CHINA CLAY.

The substance is a natural body found in this country almost exclusively in the County of Cornwall. It is found in other countries, and is known to mineralogists by its Chinese name of kaolin; it derives its name of china clay from its use in the manufacture of the white pottery called "china." China clay is prepared from the crude material and separated from the mica and quartz which is found associated with it by a process of levigation.

In chemical composition china clay is a hydrated silicate of alumina approximating to the formula $2\,SiO_2,\ Al_2O_3,\ 2\,H_2O$, and contains—

Silica, SiO_2, ...	47 per cent.
Alumina, Al_2O_3, ...	40 ,,
Water, H_2O, ...	13 ,,

but all natural clays vary a little from this typical composition, as will be seen from the analyses of several below.

ANALYSES OF CHINA CLAYS.

Constituent.	Cornwall.	China.	Laurence Co., America.	French.	Dartmoor.	Cornwall.
Silica, SiO_2, . .	46·78	50·50	47·13	48·37	47·20	46·32
Alumina, Al_2O_3, .	39·60	33·76	36·76	34·95	38·80	38·72
Water, H_2O, . .	13·16	11·22	15·13	12·62	12·00	12·67
Potash, K_2O, . .	0·12	1·90	...	2·4	1·76	0·44
Ferric oxide, Fe_2O_3,	0·09	1·80	trace.	1·26	...	0·27
Lime, CaO, . . .	0·07	...	0·04	...	0·24	0·36
Magnesia, MgO, .	...	0·80	...	...	...	0·36

It is really a decomposition product of the mineral felspar, a double silicate of alumina and potash, having the composition—

Silica, $Si\,O_2$, ...	64·20 per cent.
Alumina, $Al_2\,O_3$, . . .	18·45 ,,
Potash, $K_2\,O$, ...	17·35 ,,

and the formula $6\,Si\,O_2\,Al_2\,O_3\,K_2\,O$. By the action of the carbonic acid and water of the atmosphere this mineral undergoes decomposition with the elimination of the alkali and hydration of the alumina silicate that is left.

COMPOSITION AND PROPERTIES OF CHINA CLAY.—China clay is essentially a hydrated silicate of alumina, as has already been stated, but there are some minor differences in the composition of samples from various localities, as will be seen on examining the analyses given on p. 95; these are, of course, primarily due to differences in the composition of the granite from which the china clay has been formed, and, secondarily, to the degree of decomposition.

China clay, or kaolin, is a fine white amorphous powder, having slight adhesive properties, and adhering to the fingers when moist.

It is light, its specific gravity being about 2·24, so that it is the lightest of all the white pigments. The best qualities have a very soft unctuous feel, the common qualities are rather rougher, but none have the slightest trace of grittiness about them. The best qualities have a pure white tint, others a more or less yellowish tint, which the china clay makers are accustomed to disguise by adding a small quantity of ultramarine.

It is quite insoluble in water, dilute acids, and alkalies. Boiling in strong sulphuric acid for some time decomposes it with the formation of a gelatinous residue of silica and a solution of alumina sulphate. Hydrochloric acid has little action on it.

As a pigment it is quite permanent, resisting perfectly exposure to the atmosphere and to light for any length of time. As a pigment it is not, however, much used. In oil it loses its body and becomes more or less transparent. It can be used in water colours and in distemper work with good results, and it is used in paper-making and paper-staining. It also finds a use in the preparation of the aniline lakes, especially when these are to be used in paper-staining.

Its principal uses are for making pottery, ultramarine, finishing cotton cloths, making paper, &c.

An analysis is rarely wanted, since it is never adulterated, while for all pigment purposes absolute chemical purity is not required.

CHAPTER V.

PREPARATION OF PIGMENT COLOURS (*Continued*).

VERMILION.

VERMILION is the sulphide of the metal mercury containing—

Mercury,	. . . .	86·2 per cent.
Sulphur,	. . . .	13·8 ,,

corresponding to the formula, Hg S. It occurs naturally as the mineral cinnabar, but rarely of a sufficiently bright colour to be used as a pigment. It is obtained of a black colour on mixing mercury with sulphur, passing sulphuretted hydrogen through solutions of mercury salts, or on mixing mercury salts and soluble sulphides. It is by no means easy to make vermilion on a small scale, and even on the large scale difficulties are met with.

PREPARATION OF VERMILION.—1. Grind together 10 grammes of mercury and 3 grammes of flowers of sulphur in a mortar until a black mass is obtained. Transfer this mass to a deep clay crucible covered with a lid. Heat for five to six minutes over a Bunsen burner, then allow to cool, and open the crucible. On the underside of the lid and round the upper part of the crucible will be found a red deposit, which can be separated and tested as described below.

2. Dissolve 5 grammes of mercuric chloride in water, add a little ammonium sulphide, allow the black precipitate of mercury sulphide to settle, pour off the supernatant liquor, add a little caustic soda solution and maintain at a gentle heat for some time, adding a little water from time to time to make good any loss through evaporation. After a time the black will turn red.

It is only right to say that while vermilion can be made in this way, the experiments are not always successful.

TESTS FOR VERMILION.—Prepared in any way vermilion (mercury sulphide) answers the following tests :—

1. Heat on the lid of a porcelain crucible over a Bunsen burner. The vermilion burns away with a bluish flame and

the odour of burning sulphur (sulphur dioxide). No other red pigment behaves in the same way.

2. Treat a little in a test tube with hydrochloric acid, and also similar small quantities with nitric acid, sulphuric acid, and caustic soda. Observe that in each case it is unchanged.

3. Boil a little in a test tube with a mixture of nitric and hydrochloric acids. Observe that it is dissolved, forming a colourless solution.

MANUFACTURE OF VERMILION.—The manufacture of vermilion on the large scale follows closely on the lines of the small scale experiments given above :—

1st. *Dutch Process.*—108 lbs. of mercury and 15 lbs. of sulphur are gently heated together with constant stirring, when a black "ethiops," as it is called, is obtained. This black ethiops is next put into a deep cylindrical earthenware pot, which is arranged to be inserted to two-thirds of its depth in a furnace. This pot is covered with an iron lid, in the centre of which is a charging hole. This pot is heated to a red heat and some ethiops thrown in; when all action has ceased, more is thrown in at intervals for some hours. Then the pot is allowed to cool. On removing the lid vermilion is found as a crust on its under surface and also round the upper part of the pot. The red deposits are separated from any black portions and put on one side for further treatment, while the black parts are subjected to further furnacing. The red vermilion is ground into a paste with water, treated with a little acid, well washed in water, and dried.

2nd. *Chinese Process.*—The Chinese have long been renowned for the quality of the vermilion they make; this is attained by taking considerable care in carrying out the various operations, especially the final grinding and washing. 75 lbs. of mercury and 17 lbs. of sulphur are amalgamated together into a black or deep red mass by heating and stirring in an iron pan over a small furnace. This mass is next transferred to another iron pan, on the top of which porcelain plates are built up in the form of a dome. The whole arrangement is maintained at a dull red heat for eighteen hours, after which the pan and its contents are allowed to cool down. On pulling down the porcelain plates the vermilion is found as a crust on the under surface. The best and most brilliant coloured parts are removed and subjected to a grinding and levigating with water, so that only the finer qualities are collected. The coarser commoner qualities are again ground up and levigated, and in this way very fine grade vermilion is obtained

3rd. *Wet Process.*—68 lbs. of sulphur and 300 lbs. of mercury are ground together into a paste with water. They are then mixed with 160 lbs. of caustic potash dissolved in 100 gallons of water. This is maintained at a temperature of 45° C. for some hours, water being added from time to time to replace any loss by evaporation. After a time the black colour slowly changes to red, and when the desired shade is got the operation is stopped and the vermilion filtered off, well washed with water, and dried.

In these wet processes it is important that care should be taken not to heat the mixture of mercury, sulphur, and alkali to too high a temperature; from 45° to 50° C. is high enough. Time, not heat, seems to be the most important element to consider in these processes; too great a heat turns the vermilion brownish.

The brilliancy of fire, as it is sometimes called, of the vermilion may be increased during manufacture by—

1st. Grinding very fine and levigating;

2nd. By warming with a caustic soda lye;

3rd. By treatment with nitric acid;

4th. By treatment at about 50° C. with a mixture of caustic potash and sulphide of potassium; and

5th. By treatment with hydrochloric acid.

Any of these or a combination of them may be, and are, used for this purpose.

PROPERTIES OF VERMILION.—Vermilion is a very bright scarlet powder. It is the heaviest pigment known, its specific gravity being 8·2, which causes it to settle readily out of paints, &c., in which it is used, and renders its application somewhat troublesome. It is very opaque, and, consequently, has great covering power or body. It is quite insoluble in water, alkalies, and any single acid, but a mixture of nitric and hydrochloric acids dissolves it with the formation of a colourless solution of mercuric chloride; as a rule, very few substances are capable of acting on vermilion.

Heated in a tube out of contact with air, vermilion first turns brown, then sublimes in the form of a red sublimate.

Heated in contact with air vermilion burns with a pale blue, lambent flame, giving off vapours of sulphur dioxide and mercury oxide; if pure, there will be but a trace of ash left. Thus a sample of good vermilion analysed by the author contained—

Sulphide of mercury,	99·63
Ash,	·37
	100·00

This forms a reliable test for the adulteration of mercury, for any adulterant which may be used will be left behind on heating. The usual adulterants employed are red lead, oxide of iron, red lakes, vermilionettes, &c. The presence of any of these is easily ascertained by the application of the characteristic tests, which will be found described under each particular pigment.

When used as an oil-colour vermilion is permanent; when used as a water-colour it is generally considered to be permanent, but the experiments made by Captain Abney and Dr. Russell throw some doubt on this point. They found that vermilion used as a water-colour turned brown after two years' exposure to light and air, probably owing to an intramolecular change. Much appears to depend on the care with which the vermilion has been made.

RED LEAD.

Red lead is one of the oxides of the metal lead, and has essentially the composition—

Lead,	90·65 per cent.
Oxygen,	9·35 ,,

It is a compound of two other oxides of lead—the monoxide, $Pb\,O$, commonly called litharge; and the dioxide, $Pb\,O_2$, the puce or brown oxide of lead, the average composition being—

Lead monoxide, $Pb\,O$,	64·5 per cent.
Lead dioxide, $Pb\,O_2$,	35·5 ,,

corresponding to the formula $2\,Pb\,O$, $Pb\,O$, or more simply $Pb_3\,O_4$. By treating red lead with dilute acids, the monoxide is dissolved and converted into the corresponding soluble lead salt, while the dioxide is left behind as a dark brown, insoluble powder. There is, therefore, always a change of colour on treating red lead with dilute acids, which serves as a distinguishing test for the pigment. It is desirable to point out that the proportion of the two oxides is liable to vary in different samples of red lead, and as a rule there is a larger proportion of the monoxide than is represented by the figures given above.

PREPARATION OF RED LEAD.—It is not possible for the student to make red lead on a small scale unless he has access to a muffle furnace, in which case he can prepare it as follows:—The muffle is heated to a bright red heat, and on an earthenware saucer a quantity of lead is placed; this is allowed to melt, while a current of air is directed over the surface of the lead; this soon oxidises, and as fast as the skin of oxide forms

it is pushed on one side, so that fresh surfaces of the metal are continually being exposed to the action of the air. Care must be taken during this process in regulating the temperature, which should be just sufficient to melt the lead, but not enough to melt the oxide that is formed. When all the lead has been oxidised, the heating is continued and oxidation allowed to proceed, when the oxide or litharge first formed gradually changes into red lead. The furnace is then allowed to cool down, and the pigment so made subjected to the following tests :—

1. Treat a little in a test-tube with dilute nitric acid. Observe the production of the brown coloured oxide. Add water and filter; to the filtrate add a little ammonia, when a white precipitate of lead hydroxide, $Pb\,H_2\,O_2$, will be obtained. On adding, first, acetic acid to dissolve this precipitate, then a solution of potassium bichromate, a yellow precipitate of lead chromate (chrome yellow) is got.

2. Boil a little of the red lead with hydrochloric acid. Note that the brown oxide is first formed; that this dissolves and a colourless solution is got, from which crystals of lead chloride separate out on cooling; as also that a strong acrid gas, chlorine, is evolved while the red lead is dissolving.

3. Heat a little of the red lead with strong sulphuric acid and a little alcohol. The red lead is completely converted into the white insoluble sulphate of lead.

MANUFACTURE OF RED LEAD.—There is only one process for making red lead, which consists of two stages. The first stage has for its object the conversion of metallic lead into monoxide of lead; in the second stage this oxide is converted into red lead.

1st Stage. *Drossing.*—This is conducted in what is called the "drossing oven," a kind of reverberatory furnace; it is a low oven, open only in front, over which is constructed a hood and chimney to carry off the products of combustion, &c., from the furnace. The bed usually measures about 11 feet by 12 feet 4 inches, and is divided into three divisions. The central one measures 8 feet 4 inches wide, and constitutes the bed or hearth of the furnace; while the two side divisions measure about 2 feet each, and form the fireplaces of the oven. As a rule, they are not fitted with firebars; the partitions between the fireplaces and hearth are formed of firebrick; the bed of the furnace is made to slope from the back to the front; usually the back is about 7 inches higher than the front, while it also slopes slightly from the side to the centre. In the front of the furnace are three doors; the two side ones are for feeding the fires,

while the centre one serves for introducing and extracting the material, and for working the charge while in the furnace. It is placed a little higher than the two side doors, so that a draught is generated through the latter and out of the centre door; in the top of this door an opening is left, so that the products of combustion, &c., can pass out and up the chimney.

The operation of drossing is carried out in the following manner:—22 cwts. of lead, which is the quantity usually dealt with in one charge, are placed in the furnace, which is now raised to a dull red heat, just enough to melt the lead, the molten lead being prevented from flowing out of the furnace by the construction of a dam, formed of pieces of dross or "leanings" from previous workings, across the front of the hearth; the melted lead rapidly becomes coated with a layer of oxide, the formation of which is hastened by rabbling the lead and pushing the oxide as it is formed to the back of the furnace, the object being always to have a fresh surface of lead exposed to the oxidising action of the air which passes through the furnace. The workmen by a peculiar splashing action while rabbling expedite this oxidation very much; at intervals pigs of lead are thrown into the furnace. This drossing takes about ten to twelve hours, at the end of which time the dam across the front of the furnace is broken down, and the unmelted lead allowed to run out, while the "dross" or "casing," as it is called, is taken out to be worked for the next stage. The furnace is now ready for another charge.

The "dross" or "casing" has a rather bright yellow colour, and is coarse in texture; it consists essentially of the monoxide of lead, $Pb\,O$, but still contains some unoxidised lead. It is now ground and levigated with water; the oxide grinds to the form of a fine powder, while the lead is simply flattened out, and by sieving can easily be removed. It is sent back again into the furnace, while the ground oxide is washed by a stream of water into settling tanks, where it settles out in the form of a paste, which is ready for use in the next stage.

One point of importance in the drossing stage is to see that the temperature is carefully regulated, so that while it is above the melting point of the lead, and therefore in a molten state, yet it is below the melting point of the casing; as the margin is not great, considerable care has to be taken to avoid overstepping the limit. If the casing is allowed to melt it passes into litharge, and this cannot be converted into red lead. The dross or casing is also known as massicot.

2nd Stage. *Colouring.*—The next operation consists in heat-

ing the dross obtained in the first stage, either in the same oven or in another, which only differs from the drossing oven in a few minor details. The colouring oven is heated to a low red heat, care being taken to ensure a large supply of air. The operation takes about forty-eight hours, and the mass is frequently rabbled during that period; after it has been in about twelve hours a sample is taken out and its colour examined; this sampling is repeated at the end of each twelfth hour, and near the end of the operation more frequently. When the red lead has attained the correct colour, the fires are drawn and the furnace allowed to cool down; when cold, the red lead is drawn from the oven, ground as finely as possible, and sent into the market.

The change which takes place in the transformation of the metallic lead into red lead is shown in the following equations:—

1st Stage. $Pb + O = PbO$.

Lead plus oxygen forms lead monoxide.

2nd Stage. $3PbO + O = Pb_3O_4$.

Lead monoxide plus oxygen forms lead peroxide.

Theoretically, 100 lbs. of lead should yield 110·36 lbs. of red lead; practically about 108 lbs. of red lead are obtained, which is a very near approach to the theoretical amount. The best red lead for painters' use is made from pure lead, as the presence of impurities in the metal has a material and injurious influence on the colour of the product; iron, in particular, causes the colour to be dark. For glass makers' red lead a pure product is absolutely necessary, as an impure lead causes the glass to be coloured, not white as it should be.

PROPERTIES AND COMPOSITION OF RED LEAD.—Red lead is a heavy, bright red powder of an orange hue, its specific gravity being 8·53. Heat turns it to a dark brownish-red, but the colour is restored on cooling. Acids act on red lead. Nitric acid and glacial acetic acid first dissolve out the monoxide, leaving the dark puce oxide, which is insoluble; on further boiling, this gradually dissolves, and colourless solutions of the nitrate or acetate are formed. Hydrochloric acid when heated with red lead decomposes it with the evolution of chlorine and the formation of the chloride, which settles as the solution cools in the form of transparent needles, a very characteristic reaction of lead. Sulphuric acid boiled with red lead forms the sulphate, with the evolution of oxygen.

As a pigment red lead is very useful, it mixes very well with linseed oil, and takes from 8 to 9 per cent. of it to grind into a stiff paste. It exerts a powerful drying action on the oil; hence paint containing red lead dries very quickly; on this account, also, red lead mixed with linseed oil is largely used as a lute and packing for steam pipes and joints of all kinds. It possesses good covering and colouring power, and is capable of resisting all ordinary atmospheric influences, although it is liable to be discoloured by sulphuretted hydrogen, as is the case with all lead pigments. It may be mixed with nearly all pigments, the only exceptions being those containing sulphur, such as ultramarine, cadmium yellow, &c.

ASSAY AND ANALYSIS OF RED LEAD.—Red lead is rarely adulterated, but if so, it is usually by the oxide of iron reds.

The quantity of red lead in such an adulterated sample can be ascertained by taking 2 grammes and boiling with nitric acid until it is thoroughly decomposed; the insoluble matter can be filtered off and its amount ascertained by weighing it; to the solution, which is colourless if the red lead be pure, but yellow if there is any iron present, a little dilute sulphuric acid is added, and a precipitate of sulphate of lead obtained; this is filtered off, washed, dried, and weighed in the usual manner.

The weight multiplied by 0·955 gives the amount of red lead in the sample. The solution from the lead sulphate can be tested for iron, &c., by the usual tests.

ORANGE LEAD.

This pigment is identical in composition with red lead, but is rather paler in colour and lighter in weight. To make it, white lead is placed in a furnace similar to a red lead furnace, and heated to a low red heat for from twenty-four to twenty-eight hours, or until the mass has acquired the desired red tint. During this operation the white lead loses its carbonic acid and water, while it takes up oxygen from the air which passes through the furnace.

The change is shown in the following equation—

$$2\,PbCO_3 \,.\, PbH_2O_2 + O = Pb_3O_4 + H_2O + 2\,CO_2.$$

In washing white lead a scum collects on the top of the washing waters; this is collected and made into orange lead and gives a brighter and more bulky product than dry white lead. Orange lead has a slightly paler colour than red lead, is

more voluminous and of lower specific gravity, which is about 6·95. In its composition and properties it is identical with red lead, and it is used for very similar purposes.

KING'S YELLOW.

This yellow pigment consists of the sulphide of arsenic, $As_2 S_3$; it was extensively used before the introduction of the chrome yellows, but has since then become almost, if not quite, obsolete. This is due to the fact that it is a very poisonous compound, a property it holds in common with all arsenic preparations.

PREPARATION OF KING'S YELLOW.—Weigh out 5 grammes of white arsenic (arsenious oxide), and dissolve it by boiling in dilute hydrochloric acid. Now pass a current of sulphuretted hydrogen gas through the solution, when a yellow precipitate of arsenious sulphide, $As_2 S_3$ (king's yellow), will be obtained. This is filtered off, washed with water, dried in the usual way, and weighed.

As sulphuretted hydrogen gas will be used in preparing two or three other pigments, a few words as to its production will be of value. It is made by dissolving sulphide of iron (Fe S) in either hydrochloric acid or dilute sulphuric acid. The author prefers the former for several practical reasons; the temperature of the reacting bodies does not become so high, the resulting iron salt (ferrous chloride) is more soluble than is iron sulphate, and this is an advantage. A very convenient apparatus for preparing the gas, which is easily fitted up, is shown in Fig. 10. F is a flask of about 6-oz. capacity, while W is a bottle with a wide mouth of about 4-oz. capacity; each is fitted with a tight-fitting two-holed cork. In flask F is fitted a thistle funnel and a piece of glass tube just passing through the cork and bent at right angles, while in W are two tubes; one passes to the bottom of the bottle, while the other only just passes through the cork.

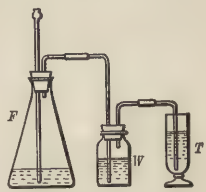


Fig. 10.
$S H_2$ apparatus.

The short tube from the flask and the long tube in the bottle, W, are connected together by a short piece of indiarubber tubing, while to the short tube from the bottle is fitted a long piece of indiarubber tubing, which forms a delivery tube to carry the gas into T, containing the arsenic solution. In T are placed the lumps of ferrous sulphide, and the acid is poured down the thistle funnel; in W is placed a small quantity of water, and the

gas which is evolved in F in passing through this is washed and freed from any of the acid liquor and iron solution which it may mechanically carry over from F. When the apparatus is finished with after being used for the experiment, the acid in F is poured away and some water poured in the bottle and this poured off. In this way the production of the gas is stopped, while what sulphide of iron is unused is kept for further use, and at the same the nuisance caused by the nauseous odour of the sulphuretted hydrogen gas is minimised as much as possible.

The reactions between the acids and the ferrous sulphide are expressed in the following equations :—

$$\begin{array}{ccccccccc} Fe\,S & + & 2\,H\,Cl & = & H_2\,S & + & Fe\,Cl_2. \\ \text{Ferrous sulphide.} & & \text{Hydrochloric acid.} & & \text{Sulphuretted hydrogen.} & & \text{Ferrous chloride.} \\ Fe\,S & + & H_2\,S\,O_4 & = & H_2\,S & + & Fe\,S\,O_4. \\ & & \text{Sulphuric acid.} & & & & \text{Ferrous sulphate.} \end{array}$$

The reaction which takes place between the sulphuretted hydrogen and the arsenious oxide is expressed in the following equation :—

$$\begin{array}{ccccccccc} As_2\,O_3 & + & H_2\,S & = & As_2\,S_3 & + & 3\,H_2\,O. \\ \text{Arsenious oxide.} & & & & \text{Arsenious sulphide.} & & \text{Water.} \end{array}$$

Having made the King's yellow, the student may make the following experiments with it :—

(*a*) Boil a little with a solution of caustic soda in a test tube, when it will be found to dissolve. On adding hydrochloric acid to this solution the yellow is precipitated.

(*b*) Boil with a little ammonium sulphide, when it will dissolve, and on adding a little hydrochloric acid it is reprecipitated.

(*c*) Boil with hydrochloric acid, in which it is insoluble.

(*d*) Try Marsh's test, as given under Emerald Green.

These tests will serve to distinguish arsenic, or King's yellow, from other yellow pigments.

CADMIUM YELLOW.

This pigment, which has a very bright yellow colour resembling chrome yellow, is the sulphide of cadmium, having a composition corresponding to the formula Cd S. It is mostly used by artists, for it is rather too expensive for ordinary house painting. It is one of the most permanent yellows known.

PREPARATION OF CADMIUM YELLOW.— Weigh

out 5 grammes of cadmium chloride, dissolve in 100 c.c. of water, and pass a current of sulphuretted hydrogen gas through the solution as long as any precipitate forms. See under King's Yellow for a description of the process of making this gas.

The reaction which occurs is represented by the equation—

$$\underset{\text{Cadmium chloride.}}{CdCl_2} + H_2S = \underset{\text{Cadmium sulphide.}}{CdS} + 2HCl.$$

The precipitate which is obtained is filtered off, washed with water, dried in the usual way, and then weighed.

It will be found to be of a bright yellow colour, to mix freely with either oil or water, and to have a good body and covering power.

The following experiments may be tried with it:—

1. Boil a little with strong hydrochloric acid, when it will dissolve to a colourless solution. Note the difference in the action of the acid on zinc and lead chrome.

2. Boil with a little caustic soda, when it will be found insoluble. Note the corresponding experiment with King's yellow above.

3. Boil with sulphuric acid, afterwards diluting with water. Note that a colourless solution is obtained, and note the difference in the case of chrome yellows. It will also be noticed that, with both hydrochloric and sulphuric acids, sulphuretted hydrogen is evolved.

These tests will serve to distinguish cadmium yellow from other yellows.

ANTIMONY ORANGE.

Antimony orange is the sulphide of the metal antimony, having the formula Sb_2S_3.

Antimony orange is now used almost solely by the india-rubber trade for colouring rubber red, it having many advantages over other orange pigments for this purpose. Chrome orange would be blackened by the sulphur which is added to vulcanise the rubber, while antimony orange is not, and at the same time it is not affected by the heat employed in the vulcanising process.

It is prepared in a similar manner to the last two pigments, by passing a current of sulphuretted hydrogen gas through a solution of antimony salt. The student should prepare a solution of antimony chloride; this he may do by boiling what is known as black antimony, the native sulphide of antimony,

in hydrochloric acid, filtering off any insoluble matter there may be. Through the solution thus prepared a current of sulphuretted hydrogen gas is passed, when antimony orange is thrown down as a bright orange-coloured precipitate, which is filtered, washed, dried slowly at a gentle heat, and weighed.

The student should try the following experiments with this product:—

1. Boil with strong hydrochloric acid, when it will dissolve to a colourless solution, from which on adding water a white precipitate of oxychloride of antimony is obtained.

2. Boil with caustic soda, when the orange will be dissolved; on adding hydrochloric acid to this solution, the orange will be re-precipitated.

3. Place a little of the orange in a porcelain basin with hydrochloric acid, add a strip of zinc, and touch this latter with a piece of platinum, the latter metal will become coated with a dark grey deposit of metallic antimony in consequence of the electric action which is set up.

It may be pointed out here that no other metal than antimony gives an orange precipitate with sulphuretted hydrogen, from a solution which contains a little free hydrochloric acid. The reaction which occurs is expressed in the following equation—

$$\underset{\text{Antimony chloride.}}{2\,SbCl_3} + 3\,H_2S = \underset{\text{Antimony orange.}}{Sb_2S_3} + 6\,HCl.$$

ANTIMONY VERMILION.

The sulphide of antimony is capable of existing in three modifications:—(1) A black or grey lustrous crystalline body, the natural product antimonite. (2) Orange powder, described above. (3) A scarlet powder. The two latter forms are prepared by precipitation. The scarlet form, or, as it may be called, antimony vermilion is but rarely made and used as a pigment.

PREPARATION OF ANTIMONY VERMILION.—14 grammes of sodium thiosulphate (the hyposulphite of the photographer) is dissolved in 25 c.c. of water; this will make a solution of about 40° Tw. in strength. Mix 10 c.c. of the ordinary commercial antimony chloride with 4 c.c. of water. The strength of this solution will also be about 40° Tw.

Place the thiosulphate solution in a beaker, so that it may be heated; pour in the antimony solution. At first a black precipitate will fall down, but this will speedily be re-dissolved and give rise to a colourless solution. The mixture is now heated

slowly; at first a yellow precipitate will appear; as the temperature rises the colour will change, passing from orange into red. When this has occurred the heating is stopped, the mass is allowed to cool, the red pigment is filtered off, washed and dried. The student may subject the precipitate to the tests given above under antimony orange, with which it is identical.

LAMP BLACK—VEGETABLE BLACK—CARBON BLACK.

It will be convenient to deal with all these blacks together because they all consist of the element carbon and are prepared essentially by one principle, the combustion in an incomplete manner of carbonaceous bodies and the collection of the sooty particles of carbon; they are sometimes denoted by the term "soot blacks."

On the small scale the preparation of these blacks may be best imitated by taking a paraffin lamp without a chimney, turning up the wick rather higher than usual, and so obtaining a very smoky flame. Hold a cold plate over the flame, and very soon a thick black deposit will be formed on the plate, which can be collected. Sufficient should be produced in this way to enable the following tests to be made:—

1. Place small portions in test tubes and treat with hydrochloric acid, caustic soda, ammonia, methylated spirit, petroleum ether. Observe that in all cases no action occurs.

2. Place a little in a porcelain or, better, a platinum crucible and heat to a bright red heat over the Bunsen burner. Observe that the black burns away without leaving any residue.

The results of the tests with acids, &c., show the indestructible character of the black, and, therefore, that it is likely to be permanent; as a matter of fact, these blacks are very permanent, while the crucible experiment shows its combustible and, presumably, carbonaceous character.

MANUFACTURE OF LAMP AND VEGETABLE BLACKS.—On the large scale these blacks are made by burning oils and fatty matters of various kinds either in lamps (whence the term lamp black) or in suitably constructed furnaces in such a manner that the combustion is incomplete and a large quantity of smoke is produced; this smoke is led into flues divided by partitions into compartments, or into a system of chambers; the smoke or soot collects on the sides of these compartments or chambers; that which collects nearest to the

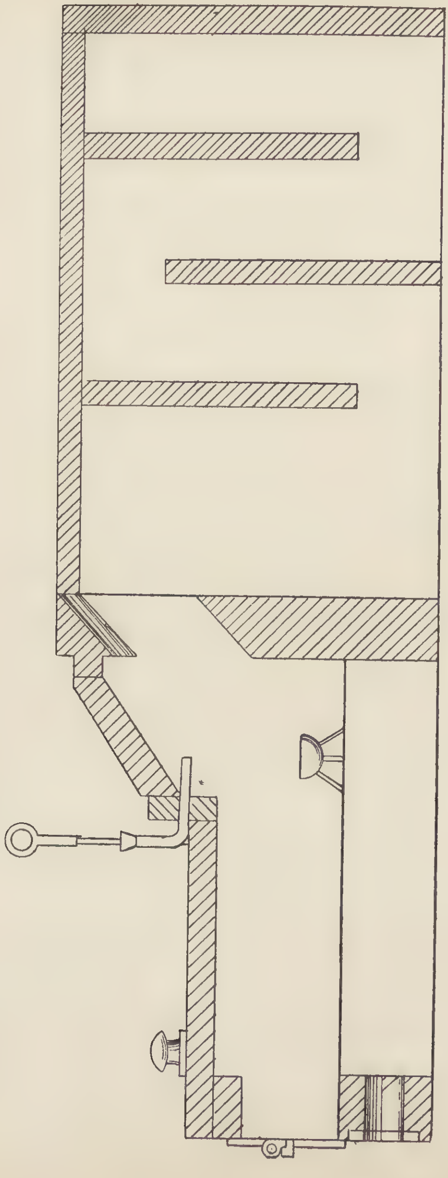


Fig. 11.—Lamp black furnace and chamber.

lamp or furnace is heavier in nature than that which collects furthest away from the lamp. The heaviest portions are called lamp blacks, the lightest portions vegetable blacks.

Fig. 11 shows a lamp black furnace with collecting chambers. An iron plate forms the floor of a furnace, and on this is an iron pot; the raw material is fed into this furnace through a pipe, the oil dropping from the end into the pot which has been previously made red hot, and so the oil burns with a very smoky flame, some of the oil dropping on the bottom plate burns away completely and serves to maintain the plate and the pot at the proper heat to burn the oil. The smoke passes through the aperture into the collecting chambers; in the first of these lamp black is collected, while in the last vegetable black is collected.

CARBON BLACK.—In America a large quantity of fine black is obtained from the natural gas which abounds to so great an extent in many districts.

The gas is burnt in specially constructed burners, and the flame is caused to impinge upon a revolving iron disc, on which the black collects and is scraped off from time to time.

PROPERTIES OF LAMP BLACK.—Lamp black is in the form of a black, flocculent powder with a fine texture; in hue it is, usually, what is termed a jet black, although some samples have a faint brownish tinge. It has great colouring and covering powers. It is rather difficult to mix with various vehicles, especially with water, but when mixed it works well as a paint; it dries rather badly when used as an oil paint, especially those samples which contain unburnt oil. It is perfectly permanent as a pigment. It is sold in the form of powder and also as a paste ground with oil, of which it takes 27 per cent., or with turps, of which it takes 55 per cent. to form a stiff paste. Vegetable black is a more voluminous black than lamp black, of a deep jet black colour and very fine texture. Its colouring and covering powers are rather greater than those of lamp black. Carbon black has similar properties to vegetable black, but has a slightly more granular structure. These blacks are used for making printing inks, varnishes, paint, and for other purposes where a fine black is required.

COMPOSITION OF LAMP BLACK.—Lamp black consists entirely of carbon, but there is a small quantity of moisture and mineral matter present in all samples. Vegetable and carbon blacks are nearly pure carbon. The following analyses of lamp and vegetable blacks will show their average composition :—

	Lamp Black. 1.	2.	Vegetable Black. 1.	2.
Carbon,	93·5	94·99	98·87	99·7
Water,	4·4	1·81	0·71	0·3
Ash,	2·1	3·20	0·42	...

Samples of lamp blacks are sometimes met with containing small quantities of oil; these come from the first condensers. Such lamp black is defective, for two reasons—1st, The oil prevents the paint made from the black drying properly; 2nd, the oil is liable to cause spontaneous combustion, so that it is no uncommon occurrence to find a cask of lamp black almost red-hot after standing some time.

CARBON BLACKS.—The carbon or gas blacks made in America are of very pure quality. Three samples examined by the author had the following composition:—

	1.	2.	3.
Carbon and occluded gases,	97·00	95·1	96·5
Moisture,	3·00	4·9	3·5
Mineral matter,	none	none	none

These blacks have small quantities (2 to 3 per cent.) of gas occluded within them; these have not been separately investigated in the above analyses.

ANALYSIS OF LAMP BLACKS.—Lamp blacks should contain but a small quantity of mineral matter, not exceeding about 3·5 to 4 per cent. To determine the amount 2 grammes should be weighed into a platinum crucible, and the black heated over a Bunsen burner until all the carbon is burnt off, and nothing but a greyish ash remains; the crucible and its contents are now weighed, and the weight of the ash ascertained. Water can be determined in the usual way. The difference between the amount of water and ash and 100 may be taken as carbon. If the black shows signs of its containing oil, the amount of this impurity may be ascertained by treating a known weight, say about 5 grammes, with petroleum ether in a Soxhlet extraction apparatus.

The petroleum ether will take out the oil; the ethereal solution is run into a weighed glass, and the ether evaporated off in the water bath; the combined weight of the glass and oil is taken, and the amount of oil ascertained. Vegetable blacks are analysed in the same way; they should have no oil, and should not contain more than 0·5 per cent. of water, or 0·25 per cent. of ash. Carbon blacks should resemble vegetable blacks in their composition.

BONE BLACK.

This black is prepared by charring bones in crucibles or a suitable furnace.

PREPARATION OF BONE BLACK.—Grind some bones into a coarse powder; fill a porcelain crucible with this, put on the lid and heat over a Bunsen burner until it is seen that no more inflammable vapours are given off. Allow the crucible to become quite cold, then open it, and it will be found that a black mass is left; this only requires grinding to be converted into a pigment. The following experiments may be tried with the pigment so prepared:—

1st. Weigh out 1 gramme into a porcelain crucible, and heat to a bright red heat over the Bunsen burner. Observe that all the black burns away and a greyish-white ash, the mineral matter of the bones, is left behind. When all the carbon is burnt off, the crucible and its contents are allowed to cool, and are then weighed. Good bone black contains 75 to 80 per cent. of mineral matter.

2nd. Take the mineral matter obtained in the last experiment and dissolve it in hydrochloric acid. Note the effervescence indicating the presence of a carbonate, and that it nearly all dissolves. Add to the solution ammonia in slight excess, when a white precipitate is obtained; filter this off, and to the filtrate add ammonium carbonate, when a white precipitate of calcium carbonate is obtained. Take the white precipitate obtained with the ammonia, add sufficient hydrochloric acid to dissolve it, then a solution of ammonium molybdate in ammonia and water, and, lastly, a little nitric acid, and boil, when a bright yellow precipitate of ammonium phospho-molybdate indicates the presence of phosphoric acid. The mineral matter of bone black consists of a mixture of phosphate and carbonate of calcium, the presence of which is indicated by the tests just given.

MANUFACTURE OF BONE BLACK.—Bone black is made on the large scale by heating bones, crushed in small pieces, in crucibles or retorts to a low red heat. It is best to use bones from which the fatty matter, but not the gelatinous matter, has been extracted. When it is seen that all volatile matter has come over, the mass in the crucible or retort is allowed to cool down, and, when quite cold, is ground up as fine as possible.

While bone black owes its colour to carbon, yet it consists

principally of calcium phosphate and carbonate derived from the mineral constituents of the bones. The following analyses, made by the author, of bone blacks will give some idea of the mineral composition :—

Water,	6·19	7·11
Ash or mineral matter,	77·97	77·75
Carbon,	15·84	15·14

The average quantity of ash contained in bone blacks is 75 per cent., of which 60 per cent. is phosphate of lime, the rest being carbonate of lime with traces of silica, iron, and alumina. The carbon ranges from 15 to 20 per cent. As a rule, the ash is white or of a pale greyish tint; sometimes it has a red tint showing that it contains iron.

PROPERTIES OF BONE BLACK.—Bone black is sent out for use as a pigment as a fine powder of a greyish-black hue, varying a great deal in various samples. It has not the brilliant hue of lamp black, nor its depth of colour. As a pigment it is quite permanent and works well in both oil and water, mixing easily with both these vehicles. It is a slow drier when used as an oil paint. The chief use to which bone black is put is in the preparation of blacking, where the large quantity of calcium phosphate and carbonate it contains gives to it properties which are as important as, perhaps even more important than, its colouring powers.

ANALYSIS OF BONE BLACK.—An analysis of it may be made in the same way as described under lamp black. The mineral matter may be further tested if there are suspicions that the sample under analysis has been made by mixing lamp black with some mineral matter. The ash which is left behind on heating the black in a platinum crucible should almost entirely dissolve in strong hydrochloric acid without much effervescence. On adding ammonia a copious white precipitate should be obtained; on drying and weighing, this should amount to about 60 per cent. of the weight of the black. To the filtrate from this precipitate ammonium oxalate should be added, and the resulting precipitate filtered off, dried, and weighed. The amount of it should be about 15 per cent. of the weight of the black. The precipitate with ammonia should be powdery, not flocculent, in appearance; the latter would indicate the presence of alumina, of which traces only are present in the ash of pure bone blacks.

IVORY BLACK is made from ivory in much the same way as bone black, and resembles it in composition and properties,

but has rather a finer hue, and is, therefore, preferred for making finer qualities of printing inks, for decorative purposes, &c.

ANIMAL BLACK is prepared by charring animal matters of various kinds. It is chiefly used in decolorising sugar, paraffin wax, petroleum oils, &c. In composition it is very variable, consisting of carbon, mineral matter, and organic matter in varying proportions.

FRANKFORT OR DROP BLACK is a black obtained by charring vegetable matter. It is a fine black, consisting chiefly of carbon, but containing a small quantity of mineral matter.

VANDYKE BROWN.

The pigment sold under the name of Vandyke brown appears to be of somewhat indefinite composition and origin. Some samples resemble the umbers in being of natural origin, but contain a quantity of organic matter. Others are obtained by the partial charring of vegetable organic matter; others, particularly those used by house painters, are mixtures of lamp black, red oxide, and a little yellow ochre.

In any case Vandyke brown is a permanent pigment, working well in oil or water.

SEPIA.—This pigment is the ink bag of the cuttle fish, particularly that species known as *Sepia officinalis*.

It is a blackish-brown pigment, mixing well with both oil and water. It is somewhat transparent, but its colouring power is great. It is a fairly permanent pigment, and is little affected by exposure to light and air. It is chiefly used by artists, particularly for monochrome work, on account of the great variety of tints and shades that can be produced with it.

CAPPAGH BROWN is a kind of umber found at Cappagh, about ten miles from Skibbereen, in County Cork, Ireland. It has a more reddish hue than umber.

CHAPTER VI.

PREPARATION OF PIGMENT COLOURS (*Continued*).

ULTRAMARINE.

THE two most important blue pigments are ultramarine and Prussian blue; the latter has already been dealt with, and the former must now be considered.

Ultramarine comes into commerce in two forms, natural and artificial; the first has been known for centuries, the last was discovered in the early part, about 1815 to 1820, of the nineteenth century; whether the two kinds are absolutely identical has not yet been established. Natural ultramarine is expensive, and, therefore, its use is restricted to artists; artificial ultramarine is cheap and finds many uses in the arts and industries, and is made in very large quantities.

NATURAL ULTRAMARINE.—In Persia, the Ural Mountains, China, and Siberia is found a blue mineral which is called lapis lazuli; it occurs in streaks and patches in a very earthy matrix. It has been used for inlaid mosaic work for many years. The pigment is extracted from the mineral by a peculiar process, which is slow and gives poor results.

Natural ultramarine, according to the analysis made by Gmelin, contains—

Silica, $Si\,O_2$,	47·30	per cent.
Alumina, $Al_2\,O_3$,	22·00	,,
Soda, $Na_2\,O$,	12·06	,,
Sulphur, S,	0·19	,,
Lime, $Ca\,O$,	1·55	,,
Sulphuric acid, $H_2\,S\,O_4$,	4·68	,,
Water and loss,	12·22	,,

It is a pigment of a very fine blue colour, quite permanent on exposure to air and light, and mixes well with oil and water.

ARTIFICIAL ULTRAMARINE.—Ultramarine is a pigment made in several shades of blue ranging from a greenish-blue shade to a violet-blue shade of considerable purity of hue. We can distinguish at least three kinds of ultramarines :—

1st. Sulphate ultramarine.
2nd. Soda ultramarine, poor in silica.
3rd. Soda ultramarine, rich in silica.

Commercially, ultramarines are sometimes distinguished as ultramarine for soapmakers, ultramarine for calico printers, ultramarine for papermakers, and so on; these differ from one another chiefly in fineness of powder and slightly in composition, as will be pointed out later on.

The raw materials used in making ultramarine are kaolin or china clay, sodium sulphate, sodium carbonate, sulphur, coal or charcoal, rosin, quartz, and infusorial earth. All of these should be of good quality, free from impurities, and finely ground.

MANUFACTURE OF ULTRAMARINE.—There are two processes in use for the manufacture of ultramarine—the indirect process, and the direct process; the first is the oldest, and by its means all kinds of ultramarine can be made; by the last, only soda ultramarine is obtainable. The manufacture of ultramarine is one of some difficulty, and reqiures considerable experience to carry out with success.

Direct Process of Manufacture.—This method can be carried out either in crucibles or muffles, the former being preferred to the latter.

Crucible Method.—The method most largely employed for the production of ultramarine is that known as the crucible method, and is carried out as follows:—

A mixture is made of—

Kaolin, ...	100 parts.
Sodium carbonate, . . .	90 ,,
Sulphur, ...	110 ,,
Charcoal, ...	20 ,,

A variable quantity of "infusorial" earth (from 20 to 30 parts) is added, according as the ultramarine has to be rich or poor in silica; in some works 6 parts of rosin are added.

A very good mixture is—

Kaolin, ...	76 parts
Sodium carbonate, . . .	60 ,,
Sodium sulphate, . . .	15 ,,
Sulphur, ...	78 ,,
Charcoal, ...	16 ,,
Infusorial earth, . . .	18 ,,
Quartz, ...	10 ,,
Rosin, ...	12 ,,

This mixture will give an ultramarine, rich in silica, of a fine shade, suitable for papermaker's use; should an ultramarine for painters' use be required that is rather poorer in silica, then the amount of infusorial earth and quartz may be reduced to about one-half of the quantities given above. It may be pointed

out that the kaolin used in making the pigment by the crucible method should not contain less than 46 per cent. of silica, while for papermaker's blue and other blues rich in silica it is advisable to select kaolin containing 50 per cent. of silica.

All these ingredients are ground together into a homogeneous mass; this is a point of great importance. The mixture is loosely packed into crucibles fitted with flat lids, which are luted on by means of mortar. When the mortar luting is dry the crucibles are piled in ovens large enough to hold from 400 to 500 crucibles. After all doors and openings into the oven are made up it is fired to a bright red heat for several hours, the length of time varying considerably and depending upon a number of factors, such as the state of the weather, the composition of the mixture, &c. Experience is the only school in which an ultramarine-maker can learn how to regulate the time required.

After the heating, all apertures are carefully closed so as to exclude air, and the furnace allowed to cool for four or five days, the oven is then opened, the crucibles withdrawn and opened, the contents turned out, and the badly burnt pieces carefully separated; the good portions are ready to be finished.

The changes which go on during the heating of the mixture are both curious and interesting. The mixture when first put into the crucibles is of a greyish colour, but during the process of burning it passes through quite a series of colour changes—brown, green, blue, violet, red, and white. The brown appears with the blue flames, due to the burning of the sulphur; it is a fine chocolate brown, but is very unstable; on exposure to the air it enters into combustion. Many efforts have been made to preserve it, but these have been fruitless. The green, which is the next change, begins to form when the sulphur has ceased to burn; like the brown, it is unstable, as the substance burns on exposure to the air. Following the green comes the blue, which is formed when the temperature has reached about 700° F., or a bright red heat; when the temperature gets higher the colour changes to a violet. With still higher temperature, first a red, then a white variety is formed. These changes are due to oxidation; when the white ultramarine is heated with reducing agents, such as carbon, the colours are re-formed in the reverse order to that in which they first appeared.

The form of furnace to be used in burning the ultramarine is not a matter of importance; the operation can be effected in a reverberatory furnace, in a muffle furnace, in earthenware pots, in ovens, or in any convenient apparatus.

Muffle Method.—A mixture of kaolin, sodium carbonate, sodium sulphate, sulphur and rosin or charcoal is made, the proportions varying in different works, but approximating to those already given.

The following mixtures work very well and yield fine blues:—

For Ultramarines Rich in Silica.

China clay,	86 lbs.
Soda ash,	60 ,,
Sulphur,	75 ,,
Sodium sulphide,	8 ,,
Rosin,	14 ,,
Infusorial earth,	4 ,,

For Ordinary Ultramarine.

China clay,	71 or 72 lbs.
Soda ash,	61 ,, 66 ,,
Sulphur,	76 ,, 78½ ,,
Sodium sulphide,	4 ,, 5 ,,
Silica,	24 ,, 24 ,,
Sodium sulphate,	4 ,, 4 ,,
Rosin,	14 ,, 14 ,,

Either mixture gives the best results when worked at a moderate red heat for from 98 to 102 hours.

The mixture reduced to the finest state so as to ensure the most intimate union of the ingredients is placed in layers of from 2½ to 3 inches thick (modern furnaces take a layer of 18 to 20 inches) and firmly pressed down on the floor of the muffle; a charge weighs about 45 lbs. The surface of the charge is covered with fireclay tiles, and the spaces between these luted with mortar; at the front of the muffle one of the tiles is left loose, so that, when required, it can be raised to admit of samples being withdrawn for testing.

The front opening of the muffle is now made up, a small aperture being left for the purpose of observing the temperature of the muffle and for drawing out samples from time to time.

The furnace is now heated, at first slowly, towards the last most strongly, so that in about eight or nine hours it has attained a dull red heat, at which temperature it is maintained for twenty-four hours, and then raised to a bright red heat until the end of the operation.

A sample is now withdrawn from the furnace through the hole in the door and a corresponding hole in the tiles; this sample is placed between two tiles as quickly as possible, and a second sample is taken out and placed on the top of the tiles;

when the samples have cooled, the colour of the samples are compared. If the operation is finished the colour of the second exposed sample will be of the blue colour, while that of the first sample (the covered one) will be of a blue-green colour; when this is found to be the case, the fires are drawn and the furnace and its contents allowed to cool down, care being taken that no air enters into the furnace, or, to make quite sure, the heat is usually maintained for another hour. Should the trial samples have a brown colour, the mass has been insufficiently heated, and the temperature of the furnace is raised a little higher.

When the furnace is opened the ultramarine is found to be in two layers, an upper one of a bright blue colour, and a lower one of a bluish-green; these are separated and finished in the usual way, the upper layer forming the best and the lower layer an inferior quality of ultramarine.

Although the quality of the blue produced by this method is good, yet the quantity capable of being produced is small; therefore it is not much use, and the crucible method described above has replaced it to a large extent.

Indirect Process of Making Ultramarine.—This consists of the two stages or operations, viz.:—

(*a*) The calcining operation.
(*b*) The colouring operation.

(*a*) **Calcining Operation—Manufacture of Ultramarine Green.**—The various ingredients are ground together with water into a very fine paste; the finer the grinding, the better will be the quality of the ultramarine; after the grinding, the paste is dried. In some works the water is omitted, it being considered unnecessary, while the subsequent drying adds to the expense of making.

The following are examples of the mixings used in different works:—

For Sulphate Ultramarine.

	1. Parts.	2. Parts.	3. Parts.
Kaolin,	100	100	100
Sodium sulphate,	83	41	220
Coal,	17	17	...
Sodium carbonate,	...	41	...
Sulphur,	...	13	30
Rosin,	...	...	35

When sodium sulphate is used less sulphur is required; in

proportion as the latter is decreased, so the proportion of the former must be increased.

For Soda Ultramarine Poor in Silica.

Kaolin,	100 parts.
Sodium carbonate,	100 ,,
Coal,	12 ,,
Sulphur,	60 ,,

For Soda Ultramarine Rich in Silica.

	1. Parts.	2. Parts.
Kaolin,	90	100
Quartz,	10	...
Sodium carbonate,	100	90
Sulphur,	60	100
Coal,	12	4
Rosin,	...	6

The second recipe gives a dark ultramarine; the more sulphur there is used in making soda ultramarines, the deeper is the shade of the blue produced ; on the other hand, by reducing the quantity of sulphur and silica the blue obtained is not so deep, but is rather more brilliant in hue.

The mixture is then placed in crucibles, being packed therein rather tightly; each crucible is fitted with a lid. The filled crucibles are piled one above the other in a kind of oven furnace, which is often made large enough to hold 200 crucibles.

After the furnace has been charged with the crucibles, the front is made up with bricks, and the interstices between these filled with a mixture of sand and clay, a small sight hole being left so that the temperature of the furnace can be observed ; if necessary, this sight hole is stopped with an easily removable plug of clay. The temperature of the furnace is then slowly raised to a bright red heat, at which it is maintained for from seven to ten hours, the time varying with the nature of the composition and determinable only by the actual practice. Sulphate ultramarine requires a higher temperature than soda ultramarine; if a muffle furnace is used, the temperature is often raised to a bright yellow for from two and a-half to three hours only.

When the calcination is considered to be complete the fire is drawn and the furnace is allowed to cool; this must be done as slowly as possible, and care must be taken that no air enters into the furnace during the cooling, because while hot the crude ultramarine is very susceptible to the action of the oxygen of

the air, and the yield as well as the shade of the colour would be injured. When cold the crucibles are removed, and the furnace is ready for another charge. This first burning of the ultramarine is a most important operation, and great care must be exercised in carrying it out; access of air to the contents of the crucible must be carefully avoided; the temperature should not be too high nor too prolonged, as then the material would be overburnt, and will not give a satisfactory blue; on the other hand, under burning is just as bad, for then the colour will not be homogeneous. A furnace can be charged three times per week.

The colour of the burnt mass varies somewhat; usually it is of a green colour, mostly of a bluish tone (which is generally indicative of good burning), but sometimes it is of a yellowish-green shade, and at others it passes more into a blue, while if not properly burnt it will have a brown shade.

The crude green ultramarine, which is somewhat cindery in appearance, is now thrown into water for the purpose of washing out all the soluble soda salts; the last washings of one batch are often used as the first wash waters of another batch for the purpose of economising the water. While still wet the ultramarine is ground up in mills into as fine a form as possible, in order to effect the completest practicable extraction of the soluble matter. The ground-up green ultramarine is then dried, when it is ready for the next operation. In this form it is sold under the name of green ultramarine for use as a pigment.

The wash waters contain a large proportion of sodium salts, chiefly in the form of sodium sulphide. In many works it is customary to evaporate the liquors to dryness by means of the waste heat of the furnaces, and to use the dry residue for another mixing.

(*b*) **Colouring Operation—Manufacture of Ultramarine Blue.**—The green ultramarine obtained in the first stage has now to be converted into the blue, which is done by heating it with sulphur in a furnace at a low temperature.

There are three ways of carrying out this colouring operation—(1) On trays, (2) in a cylinder, and (3) in a muffle.

1. *Tray Method.*—A form of muffle furnace is built, in which the muffle is filled with a number of trays or shelves. On these trays the green ultramarine is spread in layers of about an inch thick, and over them is sprinkled some sulphur; the muffle door is closed, the furnace is lighted, and the heat continued until the sulphur takes fire; then the fires are drawn and the sulphur allowed to burn itself out, after which the crude pigment is

taken from the muffle and finished in the manner described further on.

2. *Cylinder Method.*—It is also known as the *German method.* Small cast-iron cylindrical vessels are imbedded in brickwork over an ordinary fireplace; these cylinders are closed at the back end, but open at the front, which is fitted with a door made of wrought iron; in this door are two apertures for the purpose of charging the cylinder with sulphur, while a pipe from the top of the cylinder carries off the gases produced by the burning of the sulphur. An agitator is fitted to the cylinder, by means of which its contents can be kept well mixed during the progress of the operation.

From 27 to 34 lbs. of the ground green ultramarine are charged into the furnace, the door closed, and the fire lighted. When the temperature is sufficient to ignite sulphur, 1 lb. of sulphur is thrown into the cylinder; when this has burned away and fumes have ceased to issue from the cylinder, another pound of sulphur is thrown in and allowed to burn. A small sample is now drawn from the furnace and its colour noted; if not blue enough, more sulphur is thrown in and its colour noted, and this charging of sulphur is continued at intervals until a sample taken out of the cylinder shows that the blue has properly formed. After the cylinder has cooled down, the pigment is scraped into a box, and is ready for the finishing operation.

During the whole of this operation the temperature of the furnace is kept at its proper heat—viz., that at which sulphur will burn—and the agitator is kept at work.

3. *Muffle Method.*—It is also known as the *French method.* In this method the green ultramarine is coloured by heating with sulphur in a muffle furnace.

The green ultramarine is spread in a layer of about 1½ to 2 inches thick on the floor of the muffle, the door closed, and the fire lighted. When the temperature is high enough for the sulphur to burn, a shovelful of that substance is thrown into the muffle and stirred with an iron rod; when the first shovelful has burnt out, more sulphur is added from time to time, until a sample of the colour taken out of the furnace shows that it has acquired the desired blue colour. The muffle is more rapid in working than the cylinder. The blue is raked out of the furnace, and is finished in the usual manner.

The indirect process, while yielding a very good quality of ultramarine, labours under the disadvantages of making it in small quantities only at a time, and of being attended with a large loss of material in the operation.

Finishing Ultramarine.—By whatever process the pigment is prepared it comes from the furnaces in the form of a gritty, somewhat cindery-looking blue mass containing a large quantity of soluble sodium salts, and in this condition is unserviceable for use as a pigment. To fit it for this purpose the crude ultramarine has to undergo a finishing process, which has for its object to purify the colour and to develop the hidden beauty of the pigment. The process of finishing is essentially one of washing and levigation. The crude ultramarine is thrown into grinding mills, where it is ground with water, this grinding being done as thoroughly as possible, as on it depends to a very large extent the excellence of the pigment as regards colouring power and fineness.

After the grinding, the wet ultramarine is run into large tubs, where it is treated with hot water, or even boiled with water, so as to make sure that all the soluble contents of the crude ultramarine are dissolved out. The ultramarine is now allowed to settle, and the liquor run off; this contains sodium sulphate, which may be recovered by evaporation and used in making new batches of ultramarine. Then clean water is again run on to the pigment, which, after being thoroughly stirred up, is again allowed to settle and the water again poured off; this washing is repeated several times.

The wet ultramarine is now ground in grinding mills specially constructed for grinding wet materials very finely. This grinding is important, and takes several hours; the length of time depends upon the use to which the ultramarine is to be put. The finer qualities, which are used in calico printing and letterpress and lithographic printing, must be very fine, and therefore require long grinding. They are sold under the name of calico printer's ultramarine; painters do not require so fine a quality, and for this the wet ultramarine is not subjected to lengthy grinding. Another method of separating the different qualities of ultramarine is by levigation, which forms an essential part of the process.

The wet ultramarine as it comes from the grinding mills is run into tubs; that which collects in the first tub is sent back to the mills again to be re-ground with another batch of crude ultramarine. The particles which settle in the second tubs are collected, dried at a gentle heat, and sent into the market. In the water of the second tub there still remains some fine ultramarine; this is run into a third tub, where it is allowed to settle, and, after drying, is sold as a fine quality. Frequently there still remains in the last waters some very fine ultramarine,

even when the tubs have been allowed to stand for a month to settle; by adding a little lime water, which causes an aggregation of the particles, this can be collected by filtering.

Before being sold the dry ultramarine is, in many works, subjected to a process of sieving, which separates the coarser particles and yields the pigment in the form of an impalpable powder; the finer qualities should have a buttery feel when rubbed between the fingers.

The shade of the finished ultramarine depends upon several factors, such as the proportions of the constituents used in the mixings, the perfection of the burning operations, and the fineness to which the pigment has been ground; as it is impossible to regulate each of these factors with mathematical accuracy, it follows that the shade of the finished colour must vary from time to time; and as this variation is objectionable the makers overcome it by having a number of standard or type colours or shades, to which standard they bring up all batches by a process of blending and mixing different shades together so as to obtain the marketable brands.

COMPOSITION OF ULTRAMARINE.— Ultramarines are compounds of silica, $Si\,O_2$; alumina, $Al_2\,O_3$; soda, $Na_2\,O$; sulphur, S; and sulphuric anhydride, $S\,O_3$. The last, although present in almost every sample of ultramarine, is not an essential constituent of the colour.

The following are some analyses of ultramarines, mostly by the author, which will show the average composition of these important pigments :—

ANALYSES OF ULTRAMARINES.

	Sulphate.	Soap-makers'.	Calico Printers'.	Paper-makers'.	Green.
Silica, $Si\,O_2$, . . .	49·685	40·647	40·885	45·420	38·52
Alumina, $Al_2\,O_3$, . .	23·000	25·047	24·110	21·147	28·94
Sulphur, S, . . .	9·234	12·953	13·740	11·624	8·30
Sulphur trioxide, $S\,O_3$,	2·464	4·814	3·047	5·578	...
Soda, $Na_2\,O$, . . .	12·492	14·264	15·618	9·906	23·68
Water, $H_2\,O$, . . .	3·125	2·275	2·600	6·325	...
	100·000	100·000	100·000	100·000	99·44

The soapmakers', calico printers', and papermakers' ultramarines are of English make, the others of Continental make.

The analyses of papermakers' and soapmakers' ultramarines show the difference between the two varieties of soda ultramarines, the first named is rich in silica, while the other is poor in silica; the soapmakers' and calico printers' samples are evidently identical in composition, but the latter is much finer than the former. The analysis of green ultramarine shows the difference between the green and blue ultramarines.

PROPERTIES OF ULTRAMARINE.—Ultramarine is one of the most important pigments at the command of the painter. As a pigment it is perfectly fast to light and air, the only destructive agents being acid vapours which rapidly decolorise it. It can be mixed with all the ordinary vehicles used by painters and with most other pigments without being changed thereby or itself causing any change.

The only exceptions are those pigments containing lead or copper, which, owing to their forming black sulphides with sulphur, are liable to become discoloured when mixed with ultramarine; the rate of change of such mixtures as ultramarine with chrome-yellow or emerald-green is very variable; sometimes the mixture will change colour very soon; at other times the mixture will keep its colour for a considerable time; much depends upon the quality of the pigments and the care with which they have been made.

Ultramarine is distinguished by its pale but pure tone and by its tint of blue being quite different from that of all other blue pigments. The soda ultramarines are of a violet-blue shade, the sulphate ultramarine is of a pale greenish-blue tint, and is the palest blue pigment made, resembling blue verditer in tint.

The most characteristic property of ultramarines is their being readily acted upon by acids; the colour is discharged and the pigment decomposed, sulphuretted hydrogen being evolved and sulphur deposited. All acids have this property, even weak organic acids, such as acetic acid, tartaric acid, &c.; this distinguishes ultramarine from all other blue pigments; on the other hand, it prevents the use of ultramarine wherever there is the least chance of its coming into contact with acid influences, which are, sooner or later, sure to destroy the colour. Of the varieties of ultramarine, the sulphate is the most readily decomposed, while the highly silicated soda variety is the most stable of the soda ultramarines. Boiled in strong nitric acid, there is, first a decoloration, and a deposition of sulphur; afterwards the sulphur is dissolved and a residue of gelatinous silica is left behind. Alkalies have no action on ultramarine. When boiled in alum, ultramarines take a more violet tone, the sulphate

variety is the most readily changed, whilst the highly silicated soda ultramarine resists the action most; the latter variety is therefore used by papermakers, because, owing to their having to use alum, or sulphate of alumina in sizing their papers, they require an ultramarine which will not change much, if anything, under the influence of those bodies. Heat has no action on ultramarine.

ANALYSIS OF ULTRAMARINE.—Ultramarine can be distinguished from other blue pigments and detected in admixture with other pigments, by the effect which acids have upon it of decolorising it with evolution of sulphuretted hydrogen. A complete analysis of ultramarine is rarely required, but should the student desire to make such an analysis, the following scheme can be followed :—

For Water.—Heat 2 grammes in a weighed crucible for about half an hour over the Bunsen flame; the loss in weight is the amount of water present,

For Silica, $Si\,O_2$.—Treat 2 grammes with hydrochloric acid until the colour is completely destroyed; evaporate the mixture to dryness and gently ignite the residue; treat the dry mass with hydrochloric acid, filter off the insoluble silica, well wash it, then dry, and burn in a weighed crucible; the increase in weight *minus* the weight of the filter-paper ash is the weight of the silica.

For Alumina, Al_2O_3.—To the filtrate from the silica add ammonia in slight excess, boil gently, then filter, and treat the precipitate of alumina as the silica.

For Soda, $Na_2\,O$.—To the ammoniacal filtrate from the alumina add sufficient sulphuric acid to neutralise the ammonia, then evaporate to dryness in a weighed basin, and ignite the residue until all ammoniacal fumes have been given off; weigh the residue of sodium sulphate, and multiply this weight by 0·4366 to ascertain the weight of the soda, $Na_2\,O$.

Total Sulphur.—Treat 2 grammes of the ultramarine with a mixture of 2 parts of nitric acid and 1 part of hydrochloric acid until the colour is completely decomposed and only a transparent mass of silicate is left; filter this off, and to the filtrate add a solution of barium chloride in excess, boil and filter, wash the precipitate well, dry, burn, and weigh it in a crucible. To find the weight of sulphur, multiply the weight of barium sulphate so found by 0·13734; from this deduct the weight of sulphur present as sulphuric acid to find the quantity of sulphur present as sulphide.

For Sulphur and Sulphuric Acid.—Weigh out 2 grammes of

ultramarine, treat with dilute hydrochloric acid, filter off the precipitated sulphur and silica, and precipitate the filtrate with barium chloride, treat the precipitate as in the last. To find the amount of sulphur trioxide present, multiply the weight of the barium sulphate so found by 0·34335.

LIME BLUE.

This blue pigment at one time was made on a large scale, but has of later years become almost, if not entirely, disused.

PREPARATION OF LIME BLUE.—Weigh out 5 grammes of copper sulphate and 1 gramme of ammonium chloride and dissolve in 100 c.c. of cold water. Next weigh out 2 grammes of quicklime and slake in 50 c.c. of water. When both solutions are ready pour the lime solution into the copper solution and allow to stand for some time in a warm place for the blue to precipitate out; when this has happened, filter, wash, and dry the blue, care being taken that the temperature does not get too high, or the blue may be discoloured.

Test the lime blue as follows:—First treat the blue with a little ammonia, when a blue solution and a white residue will be obtained. The blue consists essentially of a mixture of copper hydroxide and calcium sulphate, these bodies being formed by interaction between the copper sulphate and the lime used, as is indicated in the following equation:—

$$\underset{\text{Copper sulphate.}}{CuSO_4} + \underset{\text{Calcium hydroxide.}}{CaH_2O_2} = \underset{\text{Calcium sulphate.}}{CaSO_4} + \underset{\text{Copper hydroxide.}}{CuH_2O_2}.$$

The copper hydroxide is soluble in the ammonia, giving a blue solution which is characteristic of copper. The calcium sulphate is not acted on by the alkali, and remains insoluble as a white residue.

Next boil the blue with a little caustic soda solution, when it will be found that the colour is destroyed, a grey product being obtained, due to the fact that the blue copper hydroxide is converted into black copper oxide.

Next boil the blue with hydrochloric acid, when it will be partially dissolved; divide the solution into two parts; to one add a solution of barium chloride, when a white precipitate of barium sulphate will be obtained, indicating the presence of a sulphate. To the other portion of the solution add first ammonia, when a deep blue solution characteristic of copper will be obtained. Now add ammonium sulphide, when a black precipitate of copper sulphide will be obtained. Now filter this off, and

to the filtrate add a solution of ammonium oxalate, when a white precipitate of calcium oxalate will be obtained, thus indicating the presence of calcium.

The manufacture of lime blue on the large scale follows on the lines of the experimental preparation given above, and does not need further detailing here on account of the obsolete character of this pigment, but reference may be made to the author's *Manual of Painters' Colours* for details.

VERDIGRIS, SCHEELE'S GREEN, AND EMERALD GREEN.

These three pigments have almost gone out of use; certainly Scheele's green has, while emerald green is used but to a limited extent as a pigment, although finding some use in agriculture as an insecticide. Verdigris, too, has but a limited use. These three pigments form a natural series, for verdigris is a basic acetate of copper, Scheele's green is the arsenite of copper, and emerald green is the aceto-arsenite of copper, and may, therefore, be regarded as a compound of the other two.

VERDIGRIS.

This pigment is the basic acetate of copper, and usually contains—

Copper oxide, $Cu\,O$, . . .	43·79 per cent.
Acetic anhydride, . . .	38·49 ,,
Water, ...	18·00 ,,

but is very variable. Some makes contain small quantities of insoluble matter. Its composition is expressed by the formula—

$$Cu\,2\,C_2\,H_3\,O_2\,Cu\,H_2\,O_2\,5\,H_2\,O.$$

In France it is made by filling large tubs with the skins of grapes, from which the juice has been expressed for wine, and sheets of copper; after a period of fourteen days or so the sheets of copper are found coated with a green deposit of verdigris which is scraped off and sold as a paint. In England plates of copper are packed between cloths soaked in vinegar. After some days the sheets of copper become coated with the verdigris, which is scraped off, washed, and dried.

By dissolving freshly precipitated hydroxide or carbonate of copper in acetic acid the normal acetate of copper, $Cu\,2\,C_2\,H_3\,O_2$,

is obtained. This acetate differs from verdigris in being soluble in water.

Verdigris answers to the following tests :—

First, heat a portion in a porcelain crucible. It will be found that the acetic acid will volatilise off, and a black residue of the oxide of copper will be left behind. This residue will be completely soluble in hydrochloric acid, giving a green solution. On adding ammonia to this there is first obtained a pale blue precipitate, which, on addition of more ammonia, dissolves to a deep blue solution. This test is eminently characteristic of copper.

Secondly, on heating a little of the verdigris or acetate of copper with dilute sulphuric acid a clear bluish solution is obtained, while acetic acid is given off, the acetic acid being distinguished by its odour. The acid solution will give the following characteristic tests for copper :—The ammonia test, as described above. On adding caustic soda a light blue precipitate of copper hydroxide, $Cu\,H_2\,O_2$, which turns into a black precipitate of copper oxide, $Cu\,O$, on boiling.

Potassium ferrocyanide throws down a brown precipitate of copper ferrocyanide. Copper acetate has the formula $Cu\,2\,C_2\,H_3O_2$, while verdigris has a composition approximating to the formula $Cu\,2\,C_2\,H_3\,O_2\,Cu\,H_2\,O_2$ with more or less water.

A quantitative analysis of verdigris may be made in the following manner :—

Weigh out 2 grammes and dissolve in a little hydrochloric acid. If there be any insoluble residue filter it off and weigh it after burning in a weighed crucible. Boil the solution and add caustic soda in slight excess, keep the solution at the boil until the blue precipitate which is first formed turns black, then filter, and wash thoroughly with hot water; to free the precipitate from every trace of alkali (which it retains rather firmly), dry the precipitate, transfer as much as possible to a weighed crucible, burn the filter paper separately and add the ashes to the main portion in the crucible, heat for half an hour over the Bunsen burner, and allow to cool when weighed. This gives the amount of copper oxide in the verdigris. By multiplying this weight by 0·798 the corresponding amount of copper is given.

The amount of acetic acid is obtained in the following manner :—Two grammes are weighed into a retort which is connected to a condenser, a small quantity of dilute sulphuric acid (5 to 1) is added, and the mixture is distilled until about three-fourths have passed over, the distillate being collected.

A small quantity of water is added to the contents of the retort and the distillation continued as before.

Care should be taken to avoid bumping; one or two small pieces of clean tobacco pipe placed in the retort will almost entirely prevent it. The distillate is taken and a little phenolphthalein added, and a normal standard solution of caustic soda is run in from a burette until a permanent red colour is obtained; the number of cubic centimetres of alkali required to bring about this change being measured. This quantity multiplied by 0·059 gives the weight of acetic acid present; 59 parts of acetic acid are equal to 39·75 parts of copper oxide. Any excess of the latter must be present as copper hydroxide in the verdigris.

SCHEELE'S GREEN.

This is the arsenite of copper having the composition—

Copper oxide, CuO,	50	per cent.
Arsenious oxide, As_2O_3,	42	,,
Water,	8	,,

corresponding to the formula—

$$Cu\,As\,O_3\,Cu\,O \,.\, 2\,H_2O.$$

It was discovered by Scheele, the Swedish chemist, in 1778.

PREPARATION OF SCHEELE'S GREEN.—Weigh out 15 grammes of arsenious oxide, the white arsenic of the shops, and dissolve by boiling in 100 c.c. of water which contain 20 grammes of sodium carbonate in the form of crystal carbonate. Next weigh out 15 grammes of copper sulphate (blue stone), and dissolve in 200 c.c. of water. When both solutions are ready, mix together, filter off the green precipitate which is obtained, wash it well, dry, and weigh it.

The Scheele's green which is thus obtained can be examined by the following tests :—

1. Boil with dilute sulphuric acid, when it will dissolve.

2. Boil with a little ammonia when a blue solution will be obtained.

3. Boil with caustic soda when a black precipitate of copper oxide will be formed.

4. Dissolve a little in hydrochloric acid and pass a current of sulphuretted hydrogen gas through the solution, filter off any precipitate which may be obtained, wash it with water, then boil for a few minutes in caustic soda solution and filter off; to the solution add a little acid when a yellow precipitate of

arsenious sulphide will be obtained, indicating the presence of arsenic. The black residue left by the caustic soda is copper sulphide and is soluble in nitric acid, the solution giving the tests for copper noticed under Verdigris.

5. *Marsh's Test for Arsenic.*—Scheele's green is arsenite of copper, Cu As O_3. The presence of arsenic gives it poisonous properties which have caused it to become obsolete as a pigment. The best test for the presence of arsenic is that known as Marsh's, which is carried out in the following manner, and depends on the fact that arsenic forms with hydrogen a gaseous compound, arsine, or arseniuretted hydrogen, As H_3:—Take a small flask (see Fig. 12), fit it with a good well-fitting cork, through which passes a thistle funnel and a piece of glass tube. The glass tube is connected with the tube, C, containing fused calcium chloride; and this in turn with a tube drawn out to a jet. This is easily done by holding the glass tube along a gas flame until it is soft enough to pull out by the fingers, turning it round while it is being heated. In the flask is placed zinc, water, and sulphuric acid, care being taken that all these substances are free from arsenic. Hydrogen will now be evolved, and will burn with a non-luminous flame at the glass jet. A light must not be immediately applied, but a few minutes should elapse so that all air be driven out of the bottle, otherwise an explosion may take place, the effects of which cannot be foretold. If a porcelain plate, B, be pressed down on the flame of burning hydrogen no effect will be observed. Now introduce a little of the Scheele's green into the flask through the thistle funnel and re-light the issuing gas, taking the same precautions as before. Now a difference in the character of the flame will be observed, it will be more bluish in tint. If a porcelain plate is pressed down on the flame a dark grey metallic looking spot will be formed, the deposit being one of metallic arsenic. This test is very delicate and will show very small traces of arsenic.

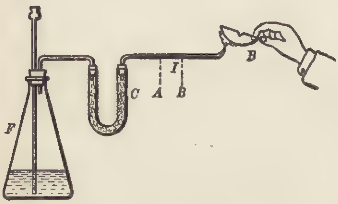


Fig. 12.—Marsh's test.

Reinsch's Test.—This is also a delicate test for arsenic. The substance to be tested is placed in a small porcelain crucible, with a little hydrochloric acid and a bright strip of copper; if any arsenic be present a grey deposit will form on the copper.

MANUFACTURE OF SCHEELE'S GREEN.—On the large scale Scheele's green can be made by boiling 20 lbs. of arsenious oxide (white arsenic), with 80 lbs. of soda crystals and 10 gallons of water; when dissolved, the solution is poured into one of 60 lbs. of copper sulphate in 40 gallons of water. The mixture is then boiled, allowed to stand for twenty-four hours, filtered, and the green washed and dried.

Scheele's green is of a pale yellowish-green colour, not very bright. It is not a good pigment; its covering power is small; it is not permanent, fading on exposure to light and air, but it is faster than verdigris or green verditer.

EMERALD GREEN.

The third of the small group of pigments is emerald green. This pigment has also been called Schweinfurth green, from the name of the place where it was first made. In America it is better known as Paris green. Emerald green is a pigment of a pale but very bright green tint, of a light bluish hue. In chemical composition it is an aceto-arsenite of copper, or it may be regarded as a mixture or combination of verdigris and Scheele's green.

There are several methods of preparing the pigment of which the student may try two or three.

PREPARATION OF EMERALD GREEN—*Method* 1.—Weigh out 12 grammes of copper sulphate (blue stone), and dissolve in 200 c.c. of boiling water; then dissolve 5 grammes of arsenious oxide (white arsenic) by boiling in a solution of 13 grammes of soda crystals in 250 c.c. of water; when both solutions are ready they are mixed together.

A precipitate of Scheele's green with a little carbonate of copper will be obtained. Acetic acid is added as long as any effervescence occurs, and then the mixture is put on one side for the emerald green to form. This will take a week or more. When formed the green is filtered off, washed, and dried, when it is ready for use.

Method 2.—A simple method is to stir 8 grammes of verdigris into a thin paste with water, and add 8 grammes of Scheele's green; place the mixture on one side for some days, stirring at intervals. When the green has formed it is filtered off, washed, and dried.

Method 3.—The methods described above are rather slow ones, requiring weeks for their completion. A much quicker process is the one devised by Prof. Galloway which is carried out as follows:—

Prepare two solutions :—1. Weigh out 12·5 grammes of copper sulphate and 16 grammes of crystal carbonate (not soda crystals); mix with about 300 c.c. of boiling water, then add sufficient acetic acid, in small quantities at a time, until the precipitate is dissolved, the reaction being assisted by heating Too great an excess of acetic acid prevents the formation of the green in the subsequent stages of the process.

2. Weigh out 7·5 grammes of arsenious oxide (white arsenic) and 4 grammes of crystal carbonate; put the two bodies in 100 c.c. of water, and boil until a complete solution is obtained. When both solutions are ready heat them to the boil, and pour the arsenic solution into the copper solution. The green forms almost immediately, and falls out as a fine green precipitate which can be filtered off, washed, and dried.

With care a very fine pigment can be prepared by this process. Do not have the solutions too strong; within certain limits, the weaker they are the finer is the character of the pigment which is obtained. Having prepared the green, the next thing is to examine it by the following test experiments:—

1. Treat a small portion in a test tube with a little ammonia, when it will dissolve with the blue colour which is characteristic of copper compounds.

2. Boil a little with caustic soda solution, when a red precipitate of cuprous oxide is obtained. No other green gives the same reaction.

3. Boil a little with dilute sulphuric acid, when the odour of acetic acid will be observed.

4. Marsh's test for arsenic, as described under Scheele's Green.

The above tests show the composition of the pigment.

The following further test can be carried out:—

5. Heat with hydrochloric acid. The green will dissolve. Dilute with water and pass a current of sulphuretted hydrogen through the solution, when a black precipitate will be obtained; filter this off, wash it with water, and then boil it with a weak solution of caustic soda. The sulphuretted hydrogen precipitates both the copper and the arsenic as sulphides; the arsenic sulphide is, however, soluble in the caustic soda solution, while the copper sulphide is insoluble. Filter off the insoluble copper sulphide; to the filtrate add hydrochloric acid, when a yellow precipitate of arsenic sulphide will be obtained. The black residue of copper sulphide can be dissolved in nitric acid; and on adding ammonia to the solution, the blue solution, showing the presence of copper, will be obtained.

The purity of a sample of emerald green may be judged by

the results of the tests given above. It may also be mentioned that the filtrate from the sulphuretted hydrogen precipitate should give no precipitate or precipitates on the successive addition of ammonia, ammonium sulphide, and ammonium oxalate, thus showing the absence of pigments prepared from iron, zinc, or lime.

Methods on the Manufacturing Scale.—Many processes have been devised for the manufacture of emerald green on the large scale, which follow in the main the lines of the small scale experiments given above. The following three processes work well:—

1. 125 lbs. of copper sulphate are dissolved in boiling water; 50 lbs. of white arsenic (arsenious oxide) are boiled with a solution of 130 lbs. of soda crystals until the arsenic is dissolved. This solution while still hot is poured into the copper solution, when a precipitate of copper arsenite will be obtained, and a little carbonate of copper also thrown down. Sufficient acetic acid is now added to neutralise all the carbonate and leave a little acid in excess. The mixture is now allowed to stand for some time for the emerald green to fully develop; in summer this may take from a week to ten days; in winter it will take about three or four weeks. When formed the green is filtered off, washed, and dried.

2. *Galloway's Process.*—In the course of an article on emerald green in the *Journal of Science,* a few years ago, Prof. Galloway described a process for the preparation of emerald green on rather more scientific lines than either of the processes formerly in use, and which gives very good results. This process is carried out in the following manner:—A quantity (100 lbs.) of copper sulphate is dissolved in water, and sufficient sodium carbonate ($28\frac{3}{4}$ lbs. of soda crystals, or $12\frac{1}{2}$ lbs. of crystal carbonate) is added to precipitate one-fourth of the copper sulphate used in the form of copper carbonate; then acetic acid is added in sufficient quantity to dissolve this copper carbonate.

There is thus obtained a solution containing copper acetate and copper sulphate in about the proportions, $3\,Cu\,S\,O_4 \,.\, Cu\,2\,C_2\,H_3\,O_2$. The copper sulphate has now to be converted into copper arsenite. To do this the requisite amount of arsenic (60 lbs.) is dissolved by boiling in sodium carbonate (38 lbs. of crystal carbonate, or $87\frac{1}{2}$ lbs. of soda crystals), which is rather less than is required to completely precipitate the copper sulphate in the first solution. The two solutions are heated to the boil, and then the arsenic solution is run into the copper solution; the green is formed immediately, and only

requires filtering, washing, and drying for use as a pigment. The quantities given above have been added by the author, and are not given in the original instructions. When carefully carried out this process gives excellent results.

The fineness of the pigment can be regulated by altering the strength of the solutions used; the weaker these are, the finer is the precipitate, and the more beautiful is the tint of the green produced. If, during the precipitation of the green, any tendency to form the yellow-green arsenite be noticed, the addition of the arsenic solution is stopped, and the mixture is boiled until all the yellow-green arsenite is converted into the blue-green emerald green.

3. *Liebig's Process.*—One part of verdigris is dissolved by heat in acetic acid, then 1 part of arsenious acid, mixed with water, is added, and a yellow-green precipitate is obtained. The mixture is boiled for some time, and the green gradually forms; if necessary, a little acetic acid should be added from time to time to ensure that all the arsenite is converted into the aceto-arsenite; too great an excess of acid, however, should be avoided, as it would decrease the yield of emerald green.

As soon as the green is fully developed it is filtered off, washed, and dried.

The drying of emerald green must be done at as low a temperature as possible, as heat causes the tint to deteriorate.

COMPOSITION OF EMERALD GREEN.—Emerald green is an aceto-arsenite of copper of somewhat variable composition, according to the process by which it has been made. The following analysis of a sample of English-made emerald green will serve to show the average composition of this pigment:—

Copper oxide, $Cu\,O$,	32·55	per cent.
Arsenious oxide, $As_2\,O_3$,	57·51	,,
Acetic anhydride, $O\,2\,C_2\,H_3\,O_2$,	6·63	,,
Sulphur trioxide, $S\,O_3$,	1·67	,,
Water, $H_2\,O$,	0·90	,,
	99·26	,,

Leaving out of consideration the impurities, the formula for emerald green deducible from the above analysis is—

$$7\,Cu\,2\,C_2\,H_3\,O_2,\ 3\,Cu\,As_2\,O_4.$$

PROPERTIES OF EMERALD GREEN.—Emerald green is a bluish-green of a very fine tone, quite different from any other known pigment, and very difficult to imitate. It is very opaque, and hence has good covering power; it works well in

both oil and water, but best in the latter. When kept in a dry place it is fairly permanent, and resists exposure to light and air, but in a damp place it turns brownish.

It is soluble in acids to blue solutions; in ammonia it also dissolves with the characteristic copper-ammonia colour; in solutions of caustic soda and potash it is also soluble; on boiling, a precipitate of cuprous oxide falls down, a characteristic reaction of emerald green.

Emerald green cannot be mixed with pigments, such as cadmium yellow, ultramarine, &c., which contain sulphur, as this causes its discolouration owing to the formation of black copper sulphide. With other pigments it can be mixed without any alteration. The use of emerald green has been on the decrease of late years, partly owing to its poisonous character, due to its containing arsenic, although one authority states that there is no foundation for the statement that emerald green is poisonous. The accounts of the poisonous action of emerald green are very conflicting; even going into a room covered with paper printed with this pigment is sufficient to produce poisonous symptoms in some persons, while others are not affected at all, so that arsenic seems to be very peculiar in its toxic action, and much depends upon the physiological idiosyncracies of the person.

ZINC GREEN.

This pigment, which is not of much importance, is a mixture of the oxides of cobalt and zinc.

PREPARATION OF ZINC GREEN.—Weigh 7 grammes of zinc sulphate and 2 grammes of cobalt nitrate, and dissolve the two salts together in 100 c.c. of water; add to this solution, as long as a precipitate forms, one of sodium carbonate. Collect the precipitate, which consists of the carbonates of zinc and cobalt, on a filter, wash well with hot water, then transfer to a porcelain crucible, and heat strongly over a Bunsen burner till the mixture turns green.

Another method is to mix 10 grammes of zinc oxide with 2 grammes of cobalt nitrate dissolved in water to a paste, then dry and heat the mixture in a crucible.

The green made by either of these methods may be tested by heating a little in a test tube with caustic soda. Note that it is not changed.

Heat a little with hydrochloric acid when it is dissolved. To the acid solution there may be added ammonia in slight excess,

when no precipitate will be obtained; then ammonium sulphide, when a grey-black precipitate, consisting of the sulphides of zinc and cobalt, will be got. On filtering this off and adding in succession to the filtrate ammonium carbonate and sodium phosphate no further precipitate should be formed. On treating the precipitate with hydrochloric acid, filtering from the black residue of cobalt sulphide, and adding to the filtrate ammonia and ammonium sulphide a white precipitate of zinc sulphide should be got. These tests are characteristic of zinc green.

The pigment is also known under the names of cobalt green, Rinman's green, &c. On the large scale the process of manufacture is on the lines of the experimental processes given above; sometimes phosphate of soda is used either instead of or in conjunction with the carbonate of soda, when the resulting pigment has a slightly bluer and brighter hue.

Zinc green has a bright green colour of a slightly yellow hue. It is perfectly permanent when exposed to light and air, mixes with all pigments, and with oil and water. It has not a strong body or colouring power. Its only good quality is its permanency.

GUIGNET'S GREEN.

The most permanent green pigment known is that variously called Guignet's green, chrome green, and viridian green, which is the oxide of the metal chromium. When well made it is of a fine green colour, with a good covering power and body.

PREPARATION OF GUIGNET'S GREEN.—Weigh out 15 grammes of boracic acid and 6 grammes of potassium bichromate, grind the two in a mortar to a stiff paste with water. Place the mass in a porcelain basin or crucible, and heat to a red heat for about an hour. Then allow the mass to cool, boil with water, filter, wash the green residue well with boiling water, and dry. Working in the small way it is not always possible to obtain the best results, and if the student does not get a good green after two or three trials he may put it down to the fact that his mode of working, or rather the conditions under which he is operating, are not quite right.

Treat portions in test tubes with hydrochloric acid and caustic soda, and observe that it is unchanged.

MANUFACTURE OF GUIGNET'S GREEN.—88 lbs. of potassium bichromate and 33 lbs. of boracic acid are ground into a stiff paste with water; the mixture is then put into a furnace where it is heated to a dark red heat for four hours.

A form of reverberatory furnace is the best that can be used. The fused mass is thrown into water and repeatedly washed by decantation, the washed pigment is ground whilst still wet under an edge runner mill, again washed, filtered, and dried.

The first wash waters contain a good deal of the boracic acid in the form of potassium borate; from this the acid may be recovered and used over again as follows:—The waters are boiled down a little, and to the liquor is added hydrochloric acid; this throws out the boracic acid, which gradually collects in the form of crystals on standing; these crystals can be collected and used for making another batch of green; in this way at least 70 to 75 per cent. of the boracic acid originally used is recovered.

Various other processes have been devised, but none are so good as the one just given.

Guignet's green consists essentially of a mixture of the hydroxide, $Cr_2 H_6 O_6$, and oxide, $Cr_2 O_3$, of chromium, the proportions of the two compounds varying in different samples.

PROPERTIES OF GUIGNET'S GREEN.—This green forms a fine green pigment of a slightly yellowish tone; it mixes well with either oil or water, has good body or covering power, and is quite permanent, being one of the best pigments which the painter can use, on which account it is much used by artists. It mixes with all other pigments without being affected by them or altering them in any way.

When properly made it is quite insoluble in either acids or alkalies. The solubility of oxide of chromium depends upon the temperature and length of time to which it has been heated; the greater these two factors are the more insoluble becomes the oxide, so that well prepared oxides are very insoluble owing to the fact that they have to be heated to a high temperature for some time.

ANALYSIS OF GUIGNET'S GREEN.—Chrome greens should be assayed for colour, brilliance, covering power, and similar properties in the usual way. When pure, chrome green should not impart a yellow colour to dilute hydrochloric acid when boiled with that reagent, such yellow colour would indicate adulteration with chrome yellow. When boiled with caustic soda chrome green should remain unacted upon. The liquor should be divided into two portions; to the one acetic acid should be added, when no yellow precipitate indicating chrome yellow should be obtained; to the other, hydrochloric acid and ferric chloride should be added, when no blue precipitate should be obtained; such precipitate would indicate the presence of

Prussian blue. Chrome greens are usually adulterated with the Brunswick greens, which adulteration is detected by the application of the two tests just given. For use by calico printers, Guignet's green is supplied in the form of a paste containing usually 30 per cent. of actual colour.

To detect Guignet's green mix a little with caustic soda and chlorate of potash in a crucible and heat strongly over a Bunsen burner. The colour will change from green to yellow, and on dissolving the residue in water a yellow solution is obtained which will give a yellow precipitate with lead acetate and shows all the reactions of chromates.

CHAPTER VII.

LAKES.

THE class of pigments known under the name of "lakes" are much used in decorative and artistic painting on account of some special properties they possess, that serves to distinguish them from some more purely mineral pigments like chrome yellow, white lead, and yellow ochre. They owe their colour to organic colouring matters or dyestuffs; in former times these were all derived from natural dyestuffs like cochineal, logwood, Brazil wool, Persian berries, &c., but in more recent years many have been made from the more numerous group of coal-tar dyes.

Lakes were first used by Italian painters and their use in painting, and their name came about somewhat in this way:—The ancient dyers who worked with kermes, &c., were accustomed to dye their goods in a bath prepared from the dye, alum and other ingredients in which the goods were boiled. On the top of this bath a coloured scum collected and painters found out that it could be used with some advantage in painting, and so this scum, "lacca," as it was called, was in much demand by them; from different dyes laccæ of various colours and shades were obtained. Soon methods were found out of preparing these laccæ separately from the dyebath, and in process of time they have taken a distinct place among artists' and decorators' pigments. From Italian "lacca," the English "lake" has been derived by easy stages.

For the preparation of lakes two essential constituents are required, a colouring principle of organic origin and a metallic oxide. The colouring principles of such natural dyes as logwood, cochineal, madder, Persian berries, quercitron bark, &c., have acid properties because they possess what the chemist calls a phenolic constitution. They enter into combination with the oxides of alumina, chrome, iron, tin, to form insoluble coloured bodies, "colour lakes," as they are called, and it is upon this property that their application in dyeing and printing of textile fabrics and in lake making is based. The colouring principles will also combine with the alkalies, soda, potash, or ammonia, but these coloured compounds are soluble in water. For infor-

mation relating to the natural dyewares and the colouring principles they contain, reference can be made to the *Manual of Dyeing* by Knecht, Rawson, and Loewenthal, or to the *Dictionary of Dyes and Mordants* by Rawson, Gardner, and Laycock, issued by the publishers of this book.

CRIMSON LAKE.—This is one of the most important lakes which are made.

The manufacture of crimson lake takes place in three stages—first, the preparation of the cochineal liquor; second, the preparation of an hydroxide of alumina; and third, the combination of these two.

Weigh out 20 grammes of cochineal and mix with 200 c.c. of boiling water and boil for five minutes; add 3 grammes of cream of tartar and boil again; then add 4 grammes of alum, boil, strain, and add to the decoction 5 grammes more cream of tartar. The cochineal liquor is ready. To prepare the alumina, weigh 42 grammes of alum and dissolve in 300 c.c. of hot water; also 14 grammes of ammonium carbonate in 200 c.c. of hot water; add the alum solution to the carbonate solution, stirring well, then filter and wash the precipitate well with hot water.

The alumina precipitate is next transferred to the cochineal liquor and the whole boiled together; when the crimson lake has formed, this is filtered off, washed, dried, and weighed.

The same method is available for working on the large scale, but using pounds in place of grammes. Various shades of lakes may be made by adding to the same quantity of cochineal liquor varying proportions of the alumina precipitate. By adding a small quantity of tin crystals to the alum it is possible to make the colour of the lake a little brighter and less blue.

Scarlet lake is made in the same way as crimson lake, but at the end a little vermilion is added.

CARMINE.—The truest type of a lake is the fine pigment carmine. In this, the colouring principle and the base are present in equivalent proportions. Several formulæ have been published for its preparation, but most of these are not accurate and will not make carmine. The following plan will yield a rich carmine:—Boil up 16 lbs. of cochineal with 1 lb. of cream of tartar in a tin vessel; strain the decoction and add to it 1 lb. of alum, $\frac{1}{4}$ lb. of quicklime dissolved in water, and $\frac{1}{4}$ lb. of skim milk. Allow the mass to stand for the carmine to separate out, which will take about five days, then filter off, wash, and dry.

In the preparation of carmine it is advisable to use tin or tinned-copper vessels for boiling the cochineal in, as a quantity

of the metal dissolves in the liquor and exerts a beneficial influence on the carmine which is produced. Earthenware vessels may be used, but iron must be avoided, as any trace of iron in solution affects the shade of the carmine rather injuriously. The use of too much alum should be avoided, as it tends to reduce the colouring power of the carmine and also to alter the tint, turning it more crimson, while the shade ought to be a scarlet.

Carmine is a deep fiery scarlet powder, slightly varying in tint, the best quality is known commercially as "nacarat carmine." It is insoluble in water, alcohol, ether, turpentine, and all the vehicles used in mixing paints, but soluble in strong mineral acids. In caustic soda, caustic potash, and ammonia solutions, it dissolves with a deep crimson colour, from which solutions the carmine can be precipitated by exposure to the air or by the addition of the weak acids, like acetic or tartaric acid; the carmine so obtained is very little changed from the original so far as tint is concerned. Solutions of salts of iron, lead, &c., have an injurious effect on the tint of the carmine. Carmine on being heated in a crucible burns and leaves behind from 7 to 10 per cent. of a white ash, which consists principally of alumina and lime.

As a pigment carmine works well in either water or oil, and is used, to a small extent, by artists as a glazing or tinting colour. It is not permanent, as a few months' exposure to sun and air is sufficient to impair the brilliancy of its hue, and prolonged exposure causes it to fade.

Carmine is frequently adulterated with other lakes and red pigments. The fact of adulteration may be ascertained by treating the lake with ammonia, when, if pure, it will completely dissolve; if not pure, the adulterant is left as an insoluble residue.

CARMINE LAKE.—In preparing carmine the liquors which are left after the carmine has been precipitated are strongly coloured; by adding to them precipitated alumina, a red lake is formed; or the addition may be alum, a little tin chloride, and carbonate of potash.

VIENNA LAKE.—This is a lake prepared from Brazil wood by the following process:—80 lbs. of starch, 20 lbs. of chalk, and 2 lbs. of gypsum are mixed with a decoction of 10 lbs. of Brazil wood; 2 lbs. of ground alum are added, and the whole well stirred together and allowed to stand for some hours; gradually the materials absorb the colour and the lake forms. When the liquor has become colourless it is decanted off and a

fresh decoction of the Brazil wood added; this is repeated until the lake becomes of the desired depth.

ROSE PINK.—To make this, 10 lbs. of Brazil wood are boiled with water and the liquor strained from the wood; there is then added $1\frac{1}{2}$ lbs. of alum, 5 lbs. of gypsum, and 10 lbs. of chalk, and the whole mass is boiled until the lake is formed.

RED LAKE.—Boil 2 lbs. of Brazil wood in water, strain, add to the decoction $1\frac{1}{2}$ lbs. of alum, 2 ozs. of tin crystals, and 2 lbs. of soda.

YELLOW LAKES.—Boil 2 lbs. of quercitron bark, strain, add to the decoction 1 lb. of alum and 1 lb. of fine whiting; boil; and, after the lake has been formed, filter and finish in the usual way. Such lakes are known under the name of Dutch Pink, Italian Pink.

YELLOW LAKE.—Boil up 1 lb. of Persian berries with 1 oz. of cream of tartar, strain, add 3 lbs. of alum, and sufficient soda to precipitate the lakes.

Similar lakes can be made from fustic, quercitron bark, and Persian berries by preparing decoctions and adding freshly precipitated alumina, boiling the whole until the lake has been properly formed.

COAL-TAR COLOUR LAKES.

Of late years very considerable attention has been paid to the production of pigment colours from the now numerous group of coal-tar dyes. The difference between a pigment colour and a dyestuff is marked not only in certain essential properties, but also in the uses to which they are put. A pigment colour must be insoluble in water and such solvents as turpentine, benzol, ether, &c., and they are applied in painting and printing with the aid of oil, gum, glue, albumen, caseine, or similar body which fixes them on to the surface to which they are applied. On the other hand, dyes must be soluble in water, and are applied to the colouring of textile fabrics woven from cotton, wool, silk, and other fibres, from aqueous solutions, being absorbed or taken up from these by the fibre, which, in some cases, is prepared or mordanted so as to enable it to properly take up the dyestuff, while in others it is not prepared in any way. But the principle really underlying the application of these dyes in the dyeing and printing of textile fabrics is the conversion of the dyestuff from a soluble substance to an insoluble form, technically called a "colour lake," either by the combination of the dye with the fibre substance of the wool,

silk, or cotton, as the case may be, or with the mordanting material which is used to prepare the fibre. If this colour lake can be produced separately from the fibre, then one can make a pigment colour which may be applied in the paint trades.

The methods by which the coal-tar colours are converted into pigment lakes must and does depend upon the chemical composition and properties of the dyestuff itself, but this is a subject which cannot be fully discussed in this book. In Messrs. Bloxam and Blount's *Chemistry for Engineers*, vol. ii., a *résumé* of the chemistry of the coal-tar colours is given.

Without attempting too elaborate a system of classification, the coal-tar colours may be divided into sixteen groups as follows :—

1. **Triphenylmethane or Rosaniline Dyes.**—Magenta, one of the earliest of the tar colours to be discovered, is a typical member of this series. It is the salt of a base known as rosaniline which has the formula—

$$C \begin{cases} C_6\,H_3\,C\,H_2\,N\,H_2 \\ C_6\,H_4\,N\,H_2 \\ C_6\,H_4\,N\,H_2 \\ O\,H \end{cases}$$

which base is supposed to be derived from the hydrocarbon methane, marsh gas, CH_4, by the substitution of two equivalents of phenylamine, $C_6\,H_5\,N\,H_2$, for two of its hydrogen atoms, of tolylamine for a third, and of hydroxyl for the fourth hydrogen atom. Another similar base is pararosaniline—

$$C \begin{cases} C_6\,H_4\,N\,H_2 \\ C_6\,H_4\,N\,H_2 \\ C_6\,H_4\,N\,H_2 \\ O\,H \end{cases}$$

which, when united to an acid, yields a crimson dyestuff that is often present in commercial magentas.

The base of malachite green and brilliant green has the formula—

$$C \begin{cases} C_6\,H_5 \\ C_6\,H_4\,N\,(C_2\,H_5)_2 \\ C_6\,H_4\,N\,(C_2\,H_5)_2 \\ O\,H \end{cases}$$

All these formulæ may be referred to the body triphenylmethane which has the formula—

$$C \begin{cases} C_6\,H_5 \\ C_6\,H_5 \\ C_6\,H_5 \\ H \end{cases}$$

Hence these dyes are often classed as triphenylmethane colours.

Starting from this parent substance, it is possible to build up magenta, and other dyes of the group, by some such series of reactions as the following :—Conversion of the triphenylmethane by the action of nitric acid into the nitro compound ; then by oxidising agents, such as chromic acid, to introduce the hydroxyl group ; and then by reducing agents to form the base, these various stages being shown in the formulæ—

$$C\begin{cases} C_6\,H_5 \\ C_6\,H_5 \\ C_6\,H_5 \\ H \end{cases} \qquad C\begin{cases} C_6\,H_4\,NO_2 \\ C_6\,H_4\,NO_2 \\ C_6\,H_4\,NO_2 \\ H \end{cases} \qquad C\begin{cases} C_6\,H_4\,NO_2 \\ C_6\,H_4\,NO_2 \\ C_6\,H_4\,NO_2 \\ OH \end{cases} \qquad C\begin{cases} C_6\,H_4\,NH_2 \\ C_6\,H_4\,NH_2 \\ C_6\,H_4\,NH_2 \\ OH \end{cases}$$

Triphenyl-methane. Nitro-triphenyl-methane. Trinitro-triphenyl-carbinol. Pararosaniline.

These bases have the peculiarity of being colourless, and it is only when they are brought into combination with an acid, such as hydrochloric or acetic acids, that they produce a coloured dye ; and it is notable that during the combination water is eliminated, so that it is not direct, as is the case of the combination of acids with bases like ammonia and aniline. The reaction is shown in the following equation :—

$$C\begin{cases} C_6\,H_4\,NH_2 \\ C_6\,H_4\,NH_2 \\ C_6\,H_4\,NH_2 \\ OH \end{cases} + HCl \quad = \quad C\begin{cases} C_6\,H_4\,NH_2 \\ C_6\,H_4\,NH_2 \\ C_6\,H_4\,NH\,HCl \end{cases} + \quad H_2O$$

Magenta contains the group NH_2 three times ; the hydrogen of this can be replaced by such organic radicles as methyl CH_3, ethyl C_2H_5, phenyl C_6H_5, benzyl C_7H_7, &c., and then other dyes are formed possessing different colours according to the character of the replacing radicle and its quantity. Thus, if it be methyl, ethyl, or benzyl, violet dyes are formed, and a range of reddish to bluish-violets are produced according as to whether one or more of the six hydrogen atoms are replaced. While if phenyl is used, then blues are obtained—reddish-blue when one or two atoms of hydrogen have been so replaced, or very pure blues when five to six atoms are replaced. Such dyes as magenta, new magenta, ethyl violet, methyl violet, Paris violet, crystal violet, brilliant green, and malachite green belong to this group of dyes.

The rosaniline dyes are what are called basic dyes, and their application in both cotton-dyeing and pigment-making depends upon the fact that when brought into combination with tannic acid they form insoluble coloured products, so that when a solution of tannic acid is added to a solution of one of these dyes a colour-lake is precipitated. Some of the so-called acid colours,

as picric acid, naphthol yellow S, &c., are also capable of precipitating this group of dyes, as will also phosphoric and arsenic acids.

When the triphenylmethane dyes are treated with strong sulphuric acid, or fuming sulphuric acid, they undergo what is called sulphonation—a process adopted for converting some of them which are insoluble, as, for instance, opal blue, the phenylated rosaniline, into soluble dyes. This process consists essentially in the introduction of an acid group of the formula $H\,SO_3$ into the dyestuff, once or more, which makes it soluble; but at the same time this sulphonation alters the dyeing properties of the dyestuff, changing it from dyes that will dye wool and silk from neutral baths into dyes which require an acid bath; hence they are known generally as acid colours, while they will no longer dye cotton satisfactorily, and again they no longer completely precipitate with tannic acid, as will be seen later on. Of such dyes, acid green, acid magenta, and acid violet are examples. Such dyes as patent blue, thiocarmine R, and fast acid green are sulphonated dyes manufactured directly.

2. **Diphenylmethane Dyes.**—These contain the group—

$$C\begin{cases} C_6\,H_4 \\ N\,H \\ C_6\,H_4 \end{cases}$$

They are but few in number. Auramine, a most valuable yellow dyestuff, having the formula—

$$C \begin{array}{l} \diagup C_6\,H_4\,N\,(C\,H_3)_2 \\ = N\,H\,H\,Cl \\ \diagdown C_6\,H_4\,N\,(C\,H_3)_2 \end{array}$$

being the best known member of the series.

All the diphenylmethane dyes are basic dyes, and are applied in lake-making with tannic acid.

3. **Nitro Dyes.**—These are colouring matters which contain the group $N\,O_2$, and are generally prepared by acting with nitric acid on organic bodies, as, for instance, picric acid, the trinitro-phenol from phenol (carbolic acid), while from naphthol are got naphthol yellow, dinitro-naphthol; aurantia, hexa-dinitro-naphthol sulphonic acid; helio-chrysine, tetra-nitro-naphthol. These dye wool and silk from acid baths, and usually give various shades of yellow. They are not good lake formers, and are not very serviceable in that capacity. Some of them, notably picric acid and naphthol yellow S, will precipitate the basic dyes, and in that way are used to make lake pigments.

4. **Nitroso Dyes.**—In the same way that by acting upon various phenols and bases with nitric acid nitro bodies are formed, so by the action of nitrous acids nitroso or, as they are sometimes called, oxime compounds are formed which contain the group NO. Examples of these bodies are dinitro-resorcine (resorcine green); nitroso-beta-naphthol, nitroso-alpha-naphthol (gambines Y and R), and nitroso-dioxy-naphthalene (gambine B). They are not a numerous group. They have the peculiarity of entering into combination with the oxides of various metals, such as iron, chrome, alumina, nickel, &c., to form insoluble coloured bodies and colour lakes, the colour of which depends not only upon the dye, but also upon the metallic oxide; thus gambines form brown lakes with chromium oxide, and green lakes with iron oxide, and upon this fact their application to the dyeing and printing of textile fabrics depends. As pigment lake-makers they are not much used, for they make only dull lakes, although these are permanent in character.

5. **The Azo-colouring Matters.**—This is by far the most important and at the same time the most numerous group of the coal-tar colours. As a matter of fact the group is divisible into several sub-groups. The peculiarity which distinguishes this group of dyes from other groups is that they contain one or more groups of two nitrogen atoms united together with two affinities shown in the formula—$N : N$—the azo group.

This is what is called in colour chemistry a chromophore—that is, a colour-carrying group; for when it is combined with two other chemical radicles, as, for instance, aniline on the one side and naphthol on the other, then a coloured compound is produced capable, under certain conditions, of acting as a dye-stuff.

When para-nitraniline ($C_6H_4NO_2NH_2$) is dissolved in hydrochloric acid and then acted upon by sodium nitrite in the cold, it undergoes a peculiar reaction. The nitrogen atom of the amido, NH_2, group of the base unites with the nitrogen atom of the sodium nitrite to form the azo group, which, combining with the organic radicle of the base and chlorine, forms a new compound called para-nitro-benzene-diazo-chloride, the formation of which is shown in—

$$\underset{\text{Para-nitraniline.}}{C_6H_4NO_2NH_2} + \underset{\text{Hydrochloric acid.}}{2HCl} + \underset{\text{Sodium nitrite.}}{NaNO_2} =$$

$$\underset{\text{Para-nitro-benzene. Diazo-chloride.}}{C_6H_4NO_2N:NCl} + NaCl + 2H_2O.$$

This reaction is typical of the diazo reaction discovered by P. Griess, which occurs when amido compounds of the aromatic organic radicles of the benzene and naphthalene series are treated with hydrochloric acid and sodium nitrite in the cold. It is generally known as the diazotising reaction, the peculiar compounds formed, as diazo compounds, while they contain, as in the instance given above, the azo nitrogen group—N : N—combined on the one hand with an organic radicle, and on the other with chlorine.

These diazo compounds are not characterised by possessing any colour, nor are they dyes. They are not stable bodies, and are decomposed by heat, exposure to light, and by standing. Their most important feature is that when brought into contact with alkaline solutions of phenols, like naphthol, or with acid solutions of bases, like naphthylamine, the phenol or base displaces the chlorine and takes its place. This reaction is shown in the equation—

$$C_6H_4NO_2N : NCl + \underset{\text{Beta-naphthol.}}{C_{10}H_7OH} + NaOH =$$

$$\underset{\text{Para-nitro-benzene-azo-beta-naphthol.}}{C_6H_4NO_2N : NC_{10}H_6OH} + NaCl + H_2O.$$

These new azo compounds thus formed are coloured and may be used as dyestuffs or colouring matters.

When the bases as para-nitro-aniline and naphthylamine and the phenols as beta-naphthol are used, the resulting azo compound is insoluble in water; this property is taken advantage of for the production of some pigment lakes, as will be seen later on, while methods of producing them direct on cotton were devised by Holliday, and are extensively used in the dyeing and printing of cotton by special processes.

By using the sulphonic acid of the bases and phenols, products soluble in water are produced, and these are extensively used as dyestuffs for wool and silk, dyeing those fibres from acid baths; they have no affinity for cotton and will do little more than stain that fibre. They can be used in the preparation of lake pigments because the sulphonic group HSO_3 gives them the property of combining with metallic oxides; they can be precipitated, therefore, by addition of metallic salts, like lead acetate, barium chloride, or alumina sulphate; or they can be combined with freshly-precipitated alumina or chromium oxides to form lakes. While this property is fairly general there are some which cannot be so used; much depends upon the number

of sulphonic groups the dyestuff contains; the more, then the less easy is it to convert them into lake pigments.

It is to be noted that the simplest azo compounds are those of the type of azo-benzene, $C_6 H_5 N : N C_6 H_5$; azo-toluene, $C_7 H_6 N : N C_7 H_6$,; azo-naphthalene, $C_{10} H_7 N : N C_{10} H_7$, and benzene-azo-naphthalene, $C_6 H_5 N : N C_{10} H_7$; these are insoluble bodies derived from the primary amines. They are not essentially coloured bodies.

The amido-azo dyes are a small group of dyestuffs which can be supposed to be derived from the simple azo compounds above noted. These have basic properties, and hence are used in dyeing by the same processes as are used with the rosaniline dyes first noticed; they can also be used in making pigment colours with the aid of tannic acid. Aniline yellow, amido-azo-benzene, $C_6 H_5 N : N C_6 H_4 N H_2$; chrysoidine, diamido-azo-benzene, $C_6 H_5 N : N C_6 H_3 (N H_2)_2$; and Bismarck brown, triamido-azo-benzene, $C_6 H_4 N H_2 N : N C_6 H_3 (N H_2)_2$, are the best known examples, and it is to be noticed that their basicity increases at the same time as the number of amido groups increases, while their colour shows a regular gradation from yellow through orange to brown with the same increase of amido groups.

The two naphthols, alpha- and beta-naphthol, $C_{10} H_7 O H$, and their sulphonic acids, of which many are known, are very important constituents of azo dyes, and they combine with diazotised aniline and its homologues to form a well recognised series of dyestuffs, of which the following may be taken as examples:—

Orange G T, benzene-azo-beta-naphthol-disulphonic acid, $C_6 H_5 N : N C_{10} H_4 O H (Na S O_3)_2$; ponceau G T, toluene-azo-beta-naphthol-disulphonic acid, $C_7 H_7 N : N C_{10} H_4 O H (NaS O_3)_2$; scarlet G, xylene-azo-beta-naphthol disulphonic acid, $C_8 H_9 N : N C_{10} H_4 O H (Na S O_3)_2$; ponceau 3 R, cumine-azo-beta-naphthol-disulphonic acid, $C_9 H_{11} N : N C_{10} H_4 O H (Na S O_3)_2$.

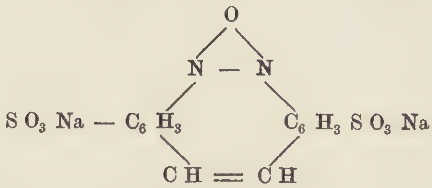
It may here be stated that the dyes are sent out as sodium salts of the sulphonic acids of the dyes as shown in the above formulæ.

It will be observed that in such a series of dyes as the one just noticed there is a regular gradation of colour from orange with the orange G T, through reddish-orange, scarlet to bluish-scarlet, in the ponceau 3 R, as one of the higher homologues, toluidine, xylidine, and cumidine, if aniline is used as the base from which the dye is made. The same thing is to be noted in connection with the range of chromotrops.

When the dyestuffs contain the azo group—N : N—once, they are called mono-azo-dyes; some are known which contain it twice, and of these there are at least two well-marked groups, one known as dis-azo dyes, of which Biebrich scarlet is one of the earliest and best known types; these are derived by first diazotising a base or its sulphonic acid, combining with another equivalent of base or sulphonic acid of a base, again diazotising and combining with a naphthol or its sulphonic acid. Biebrich scarlet is the sodium salt of benzene sulphonic acid—azo-benzene sulphonic acid—azo-beta-naphthol, $Na\,S\,O_3\,C_6\,H_4\,N : N\,C_6\,H_3\,Na\,S\,O_3\,N : N\,C_{10}\,H_6\,O\,H$; while croceine scarlet is the sodium salt of para-benzene sulphonic acid—azo-benzene azo-beta-naphthol sulphonic acid, $C_6\,H_4\,Na\,S\,O_3\,N : N\,C_6\,H_4\,N : N\,C_{10}\,H_3\,O\,H\,S\,O_3\,Na$. Many of these disazo dyes have a slight affinity for cotton and may be used to dye that fibre; but, as a rule, the colours so got are not fast to washing. Another group of dyes is obtained from bases like benzidine, toluidine, dianisidine, which contain two of the amido, $N\,H_2$, groups, and hence when these are diazotised they yield dyes with two azo groups; generally these are called tetrazo colours. Typical members of this group are Congo red from benzidine and naphthionic acid; benzo-purpurine, from oluidine and naphthionic acid; benzo-azurine, from benzidine and naphthol sulphonic acid; diamine scarlet B, from benzidine naphthol disulphonic acid and phenol ethyl-ether. Nearly all the members of this group have a strong affinity for cotton, and will dye that fibre from plain or neutral baths; hence they are known as the Direct Cotton Colours, and are now very numerous, although the first, Congo red, was only introduced in 1885.

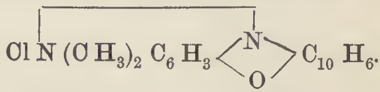
Some few dyes contain three (triazo or trisazo dyes) of the azo groups. These, as a rule, are dull violet or blue, and may even appear black in full shades. Naphthol black, acid black, and wool black are examples of such dyes. Some of the azo dyes are obtained from such bodies as salicylic acid, cresotinic acid, amido-salicylic acid, di-hydroxy-naphthalene, mono- and di-sulphonic acids, chromotropic acid, &c., which contain hydroxyl groups. These have been found to have a strong affinity for metallic oxides, and so may be used for dyeing wool and silk fibres mordanted with chrome or alumina oxides in fast colours. They are known as mordant dyeing azo colours, and are exceedingly useful in calico printing, wool dyeing, &c., and are capable of being used in pigment lake-making with chromium and aluminium oxides. Examples of the use of the azo dyes in the making of lake pigments will be given presently.

6. **Azo-oxy Dyes.**—This series of dyes contains the group N — O — N, which takes the place of the azo group in the last series, and they are used much in the same way. Some of them are direct dyes for cotton. Curcumine S, which is the sodium salt of azo-oxystilbene-disulphonic acid, having the formula



is the best known example.

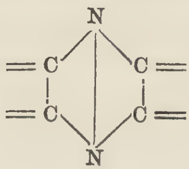
7. **Oxazine Dyes.**—Of these there are but few. Meldola's blue is the original type of this group which contains the group N O connected with a dyad radicle on each side. Meldola's blue is the chloride of dimethyl-phenyl-ammonium-beta-naphthoxamine, having the formula



Nile blue is of a more complex composition, and contains the oxazine troup twice.

All the dyes of this group are basic colours, dyeing cotton on a tannin mordant, and wool and silk direct without a mordant, and giving, as a rule, fine fast shades. They are used with tannic acid in making pigment lakes.

8. **Azine Dyes.**—The characteristic feature of these dyes is the possession of a group of two nitrogen atoms and four carbon atoms arranged in a ring form, as shown in the formula—



Belonging to this group are the saffranines, Magdala red, and one or two other dyes. They are basic dyes, some of them containing free amido groups, dyeing cotton in a tannin mordant in fairly fast shades; for this fibre they have a weak affinity, and can be used as direct colours for producing pale tints. They

undergo diazotisation, and can then be combined with beta-naphthol to form basic dyes, such as naphthindone B, indoin, diazine blue, and vacanceine blue, while the range of Janus dyes are produced from saffranines in a similar manner, and these have the property of dyeing cotton either on a tannin mordant or from weak acid baths.

9. **Induline Dyes.**—Closely allied to the azine dyes are the indulines and rosindulines, which contain two nitrogen atoms connecting together two organic radicles, the parent bases from which the induline dyes are derived being benzene induline, $C_6H_4 \left\langle {N \atop N} \right\rangle C_6H_4$, from which the commercial indulines and nigrosines are derived; naphtha-phenazine, $C_{10}H_6 \left\langle {N \atop N} \right\rangle C_6H_4$, from which the rosindulines and azine green are derived; and naphthazine, $C_{10}H_6 \left\langle {N \atop N} \right\rangle C_{10}H_6$, from which naphthyl blue and naphthyl violet are derived. They are essentially basic dyes, but the parent dyestuffs are insoluble in water, and so the commercial products are the sodium salts of the sulphonic acids of these bodies; they are used to dye wool and silk from acid baths. Some of them will dye tannin-mordanted cotton. As a rule, the induline dyes are very fast.

10. **Thionine or Thiazine Dyes.**—This group resembles the oxazine dyes, but they contain the group $\frac{N}{S}$. Methylene blue, Lauth's violet, methylene green, and new methylene blue belong to this group. They are basic dyes, dyeing on to silk and wool direct from neutral baths, and cotton on a tannin mordant. The shades produced have a fair degree of fastness. With tannic acid they give pigment lakes.

11. **Indophenols.**—The commercial indophenol has the composition shown in the formula—

$$N \left\{ \begin{array}{l} C_6H_4N \, . \, (CH_3)_2 \\ C_{10}H_5O \end{array} \right.$$

It is insoluble in water, but by the action of reducing agents it is converted into indophenol white, which is practically colourless; by oxidation the blue indophenol is reproduced. On this property is based the use of this dyestuff in dyeing blue on

wool or cotton. It is, however, not much used, and not at all in lake-making.

12. **Eurhodine Dyes.**—Of this group but few members are known, neutral red and neutral violet being the best known. They are basic dyes of no great importance.

13. **Fluorescein Dyes.**—Fluorescein is a compound obtained by combining resorcinol with phthalic acid, and it has the formula—

$$C_6H_4 \left\langle \begin{matrix} CO\,C_6H_3OH \\ CO\,C_6H_3OH \end{matrix} \right\rangle O$$

It is characterised by its solutions having a strong yellow-green fluorescence by reflected light. By the action of bromine, iodine, and nitric acid it is converted into colouring matters, which, in the form of potassium, calcium, or sodium salts are used as dyes under the names of eosine, erythrosine, phloxine, rose bengale, &c. These are all brilliant reds, dyeing wool and silk from acid baths in very bright shades from scarlet to crimson, which unfortunately lack something in fastness, especially to light. They are excellent lake makers, for they combine with alumina, lead, tin, or chromium oxides to form insoluble coloured lakes, which form the basis of the common royal reds, vermilionettes, imperial reds, &c. Of these several examples will be given later on.

14. **Anthracene Dyes.**—The coal-tar hydrocarbon, anthracene, $C_{14}H_{10}$, by suitable oxidising processes can be converted into anthraquinone, which has the formula $C_6H_4 < {}^{CO}_{CO} > C_6H_4$. This can be made to take up two or more hydroxyl groups, and thus it is converted into alizarine, dihydroxy-anthraquinone, $C_6H_4 < {}^{CO}_{CO} > C_6H_2(OH)_2$; purpurine, trihydroxy-anthraquinone, $C_6H_3OH < {}^{CO}_{CO} > C_6H_2(OH)_2$; alizarine Bordeaux, tetrahydroxy-anthraquinone, $C_6H_2(OH)_2 < {}^{CO}_{CO} > C_6H_2(OH)_2$; alizarine cyanine, pentahydroxy-anthraquinone,

$$C_6H\,.\,(OH)_3 < {}^{CO}_{CO} > C_6H_2(OH)_2.$$

All these bodies, owing to the hydroxyl groups they contain, can combine with the oxides of the metals tin, aluminium, chromium, and iron to form colour lakes. They are not dyes

of themselves, and it is only when they are brought into contact with these oxides that they form colours, which varies not only with the dyestuff but with the particular oxide used; thus alizarine with alumina gives a scarlet, with chrome a dark red, and with iron a dark violet. This property of the alizarine dyes, as they are called, can only be utilised by preparing or "mordanting" the various textile fibres with the mordanting oxide; hence they are often called "mordant dyes." They are characterised by producing fast but not bright colours. As a rule, they are not good lake makers, although it is possible to make some good and permanent lakes by their means.

The above is perhaps but an imperfect attempt to classify the coal-tar colours into groups, but it will suffice for the present purpose.

When any of these dyes are used along with a precipitating agent alone, a pure lake is formed; but, with very few exceptions, such are not commercially made or used, for they are too costly and often the true colour of the dye is not developed; some of them, as, for example, magenta and violet, have the property of appearing green when in a concentrated form, and it is only when they are diluted down that their characteristic colour becomes evident. Therefore the commercial lakes are mixtures of the pure lake with some white pigment or "base," such as precipitated alumina, barytes, precipitated barium sulphate, gypsum, whiting, &c.; in the case of vermilionette and royal reds orange lead is used as the base, either alone or in conjunction with barytes. There is not much difficulty in making these lakes, and the methods adopted will be best seen by preparing a number on a laboratory scale; from the results obtained the method of making on a large scale can be readily inferred.

PREPARATION OF MAGENTA LAKE.—Weigh out 50 grammes of barytes and mix with sufficient boiling water, say, 250 c.c.; add to the mixture 1·5 grammes of magenta, stir well, and, when the dye has dissolved, add 2 grammes of tartar emetic, then a solution of 3 grammes of good quality tannic acid previously dissolved in 50 c.c. of hot water. The magenta lake will be almost immediately thrown out, and, on allowing it to settle, the clear top liquor should be free from colour, or, at the most, have only a faint pink tint. If it is strongly coloured it is an indication that sufficient tannic acid has not been added. In making these lakes a good way of examining the mixture to see if sufficient precipitant has been added is to dip a narrow strip of blottingpaper into the mixture for a moment and then

withdraw it. If the precipitation be complete there will be a sharp line at the point to which the paper had been dipped into the mixture. But if sufficient precipitant has not been added then above this point coloured streaks will rise in the paper from capillary attraction. The barytes is simply an inert body, and has little or no effect on the precipitation of the lake beyond that the latter becomes diffused through it. It is important that during the time the tannic acid is being added the mixture should be kept well stirred, so that the precipitated lake gets well and uniformly diffused through the barytes, or otherwise the resulting pigment will have some white streaks about it.

The precipitating agent is the tannic acid, and there should be a definite relationship between the quantity of magenta used and that of the tannic acid required, but unfortunately the commercial articles are not always of a regular strength, so that definite quantities cannot be given. C. O. Weber has made some experiments on this point with pure dyestuffs and tannic acid of known strength, and his results are given in the *Journal Soc. Chemical Industry*, 1891, p. 896, to which reference can be made.

The tartar emetic is not absolutely essential to the formation of the lake, but it improves its quality. In the first place the antimony it contains enters into union with the tannic acid and forms an insoluble antimony tannate, which combines with the dye to form a sort of triple combination lake, which is more insoluble and more resistant to light and weather than the simple combination of dye and tannic acid.

Moreover, in the reaction between the tannic acid and the magenta some free hydrochloric acid is liberated, and this tends to prevent proper precipitation of the colour lake; when tartar emetic is used, then the hydrochloric acid reacts with this and is neutralised; free tartaric acid is liberated, but this has no material influence on the precipitation of the lake. Sometimes, with this object in view, sodium acetate is added by some lake-makers, but the use of tartar emetic is far preferable, because sodium acetate will not form an insoluble tannate, while, as pointed out above, tartar emetic does.

Magenta may be taken as the type of the group of basic or tannic colours which can be converted into lakes by the use of tannic acid and tartar emetic. A few examples will now be given, but it is impossible to speak specifically of the use of all known basic colours, and so only the best of the class can be named.

Yellow Lake.—100 grammes of barytes, 5 grammes of tartar

emetic, 3 grammes of auramine II., and $7\frac{1}{2}$ grammes of tannic acid.

Green Lake.—100 grammes of barytes, 3 grammes of tartar emetic, 2 grammes of brilliant green, and 4 grammes of tannic acid.

Pea-Green Lake.—100 grammes of barytes, 1 gramme of brilliant green, 2 grammes of auramine, 3 grammes of tartar emetic, and 5 grammes of tannic acid. This is an example of the use of a combination of two of these basic dyes in the production of a lake; it may be pointed out that by varying the proportions of the two dyes it is possible to make a number of lakes varying in tone from a yellow-green to a blue-green.

In place of auramine there may be used benzoflavine or thioflavine T, but these give different shades of yellow lakes; in place of brilliant green there may be used malachite green, or methyl green or methylene green; these give somewhat bluer shades of lake than does brilliant green.

Blue Lake.—100 grammes of barytes, 3 grammes of tartar emetic, 3 grammes of methylene blue, and 6 grammes of tannic acid. By using the new methylene blues a range of blue lakes, varying in tone from a reddish-blue to greenish-blue, can be made.

Violet Lake.—100 grammes of barytes, 2 grammes of tartar emetic, 2 grammes of methyl violet, and 3 grammes of tannic acid. The methyl violets are made in many brands, 3 R to 6 B, and by using these quite a range of lakes, varying in shade from a purple to a pure violet, can be made.

Dark Blue Lake.—100 grammes of barytes, 3 grammes of tartar emetic, 3 grammes of naphthindone B, and 6 grammes of tannic acid.

Crimson Lake.—100 grammes of barytes, 3 grammes of tartar emetic, 3 grammes of safranine, and 6 grammes of tannic acid.

Brown Lake.—100 grammes of barytes, 3 grammes of tartar emetic, 3 grammes of Bismarck brown, and $4\frac{1}{2}$ grammes of tannic acid.

Scarlet Lake.—100 grammes of barytes, 3 grammes of tartar emetic, 1 gramme of safranine, 2 grammes of auramine, and $4\frac{1}{2}$ grammes of tannic acid.

Among other basic dyes suitable for making lakes are acridine yellow, acridine orange, tannin orange, acridine red, new blue, new phosphine, indazine M, methyl indone, methylene violet, Basle blue, Nile blue, anisoline, rhodamine (excellent for pink lakes), azine green, Capri blue, Capri green, chrysoidine, clema-

tine, cresyl blue, cresyl violet, crystal violet, ethyl violet, neutral violet, flavinduline O, indamine, indoin, metaphenylene blue, new fast blue, neutral red, pyronine, and rhoduline red.

Green Lake.—Weigh out 50 grammes of barytes, 1 gramme of naphthol yellow S, and ½ gramme of brilliant green, and mix with a suitable quantity of water; then add 5 grammes of barium chloride; observe that the green is not precipitated; next add 3 grammes of tartar emetic and 2 grammes of tannic acid. Filter off and finish the lake in the usual way. The barium chloride serves to precipitate the naphthol yellow S, but has no action on the green, which is precipitated in turn by the tannic acid. Naphthol yellow S is not a satisfactory lake dyestuff, Indian yellow is rather better.

Similar combinations of basic and acid dyes are sometimes employed in the preparation of lakes, but they are not quite satisfactory. The lake made after the manner given above becomes yellower on exposure to air, due to the fugitive character of the brilliant green.

Blue Lake.—Weigh out 50 grammes of barium sulphate and 2 grammes of patent blue V, add 4 grammes of barium chloride, then 2 grammes of soda, 2 grammes of tartar emetic, and 4 grammes of tannic acid. Filter, wash, and dry the lake in the usual way. Patent blue V belongs to a type of dyestuffs which consist essentially of sulphonated basic dyes; tannic acid only partially precipitates such dyes, and it is necessary to employ barium chloride or alumina sulphate to complete the precipitation; these latter combine with the sulphonic groups, while the tannic acid combines with the amido groups of the dyestuffs. Alkali blue, soluble blue, patent blue, acid green, acid violet, formyl violet belong to this type of dyestuff; they are by no means good lake makers, although they give bright lakes, for they are not completely precipitated; some of them are exceedingly difficult to precipitate. They are not employed in the preparation of lakes, for they are not permanent on exposure to light; ultramarine and Prussian blue make more satisfactory pigments.

Scarlet Lake.—Example 1.—Weigh out 100 grammes of barytes, 3 grammes of scarlet R; mix with water; heat to 180° F., and add 10 grammes of barium chloride dissolved in sufficient water; filter off the precipitated lake, wash, and dry it. Scarlet R is the type of the azo group of dyes, of which there are too many to name in detail. The best manner of precipitating them is with barium chloride, as in the above instance, but lead acetate and alumina sulphate are frequently

used as precipitants; some, of course, will form a lake easier with lead than with barium, others with alumina than either of the other precipitants.

Example 2.—Dissolve 6·25 grammes of Glauber's salt and 1 gramme of scarlet R in sufficient water; heat to near the boil, then add a solution of 7 grammes of barium chloride; filter off the precipitated lake, wash, and dry it in the usual way. In this method of working the barium chloride forms not only a colour lake with the dye, but also barium sulphate by interaction with the Glauber's salt (sodium sulphate), and this forms the base on which the lake is precipitated. Lakes made with this process are much finer and more brilliant in tone than those made with barytes, but they cost more.

Example 3.—Mix together 100 grammes of barytes, 4 grammes of croceine scarlet M, and 12 grammes of lead acetate. In some cases with croceines complete precipitation does not occur, but the addition of a little ammonia will bring it about.

Example 4.—56 grammes of china clay are mixed with 10 grammes of scarlet R, then with 100 grammes of alumina sulphate, then with a solution of 35 grammes of sodium carbonate, and, after stirring well, with a solution of 100 grammes of barium chloride. In this case the lake is made on a compound base of china clay, alumina hydroxide (formed by reaction between the aluminium sulphate and the sodium carbonate), and barium sulphate (formed by reaction between the sulphate and the barium chloride). This method of making lakes will be found an excellent one, leading to the production of brilliant lakes, much more so than can be got by simply mixing the dyestuff, inert base, and precipitant together, but they are more costly; care must, however, be taken not to add too much carbonate of soda.

Brilliant Scarlet Lake.—Dissolve separately, 1 gramme of eosine A, 10 grammes of croceine scarlet M, 33 grammes of Glauber's salt, 25 grammes of barium chloride, and 16·5 grammes of lead acetate. When all are dissolved, mix the two dyes and the Glauber's salt together, then add the lead and barium salts together, filter, wash, and dry the lake.

There are various brands of scarlets, such as R, G, 2 R, OOO, and croceines 3 B; by using these, either alone or mixed together, lakes of different tints can be made.

Orange Lake.—100 grammes of barytes, 5 grammes of orange G, and 10 grammes of barium chloride. There are various brands of orange dyes, such as orange extra, E N Z, R, &c., which give various tints of orange lakes.

Yellow Lake.—Example 1.—100 grammes of barytes, 3 grammes of tartrazine, and 10 grammes of barium chloride.

Example 2.—100 grammes of barytes, 3 grammes Indian yellow, and 5 grammes of barium chloride.

Brown Lake.—Example 1.—100 grammes of barytes, 3 grammes of orchil brown B, and 6 grammes of barium chloride.

Example 2.—62 grammes of Glauber's salt, 10 grammes of cotton brown A, and 85 grammes of barium chloride.

Mauve Lake.—100 grammes of barium chloride, 3 grammes of acid mauve B, and 15 grammes of barium chloride.

Violet Lake.—62 grammes of Glauber's salt, 10 grammes of formyl violet S 4 B, and 85 grammes of barium chloride.

In most of the above lakes, barytes has been used as the base on which to precipitate the lake, but in place of it china clay, gypsum, or other inert white base may also be used, and it is good practice for the lakemaker to produce lakes from these bases and note any difference in depth of tint.

Vermilionettes.—These useful pigments owe their brilliant colour essentially to eosine; the best brands to use are eosine A and eosine 3 G, precipitated with lead acetate on, usually, a combined base of orange lead and barytes, although frequently only orange lead is used; in the latter case the pigments often pass under the names of royal reds, imperial reds, &c. These lakes are made in the following manner:—

Pale Vermilionette.—Weigh out 100 grammes of barytes and 30 grammes of orange lead, mix with about 500 c.c. of water, add 2 grammes of eosine 3 G, stir well, heat to 180° F., and add a solution of 6 grammes of acetate of lead in 50 c.c. of water. Finish in the usual way.

Deep Vermilionette.—This is made after the same manner from 100 grammes of barytes, 30 grammes of orange lead, 6 grammes of eosine 3 G, and 16 grammes of acetate of lead.

Deep Vermilionette.—100 grammes of barytes, 8 grammes of eosine 3 G, and 20 grammes of lead acetate. In this no orange lead is used.

Pale Royal Red.—100 grammes of orange lead, 4 grammes of eosine 3 G, and 10 grammes of lead acetate.

Deep Royal Red.—100 grammes of orange lead, 8 grammes of eosine 3 G, and 20 grammes of lead acetate.

It will not be necessary to give any more formulæ, as based on the lines indicated in the above the lakemaker can vary them to a great extent. By using other brands of eosine than that named, the various brands of phloxines, erythrosines, and rose bengale, the tint of the vermilionettes, royal red, or what-

ever name be given to the pigment, can be varied greatly; while the various eosines, &c., can be mixed together. In place of using lead acetate, alum or sulphate of alumina may be used; the alumina-eosine lakes so formed are somewhat bluer in tint, but are not so permanent as the lead-eosine lakes. It may be pointed out that the lakemaker should be prepared to vary the amounts of lead acetate or alumina sulphate used to precipitate the lake according to the strength and brand of the dye used. An excess of precipitant is not desirable.

Eosine Lake.—Dissolve, separately, in water 3 grammes of eosine 3 G, 50 grammes of barium chloride, and 50 grammes of alumina sulphate. Run the two latter solutions simultaneously into the eosine solution, then the lake precipitates out. A very fine pigment can be made in this way.

PROPERTIES OF VERMILIONETTES AND ROYAL REDS.—As pigments they are very brilliant in hue and have a good depth of colour, whether used as oil colours or as water colours, as well as good body or covering power. For colouring spirit-varnishes they are not good, as the eosine they contain is somewhat soluble in the spirit, and, consequently, the pigment loses its brilliant colour. One fault which they may have is that of blooming, due to the solubility of the colouring matter in the vehicle, this generally happens when insufficient lead acetate has been used to precipitate the eosine; in such cases the pigment usually contains some traces of free eosine, which passes into the vehicle and causes blooming.

They do not resist lengthened exposure to light and air; hence, for work which must have permanence, they cannot be recommended, still they will, if well made, stand a good deal of exposure, more especially if protected by a coat of varnish.

Vermilionettes and royal reds may be recognised by their greater or less solubility in alcohol, and by the solution showing a fluorescence, the character and colour of which will depend upon the particular eosine used in their preparation. Heat destroys the colour; if eosine and barytes alone have been used in preparing the pigment then the colour will be completely destroyed, but if orange lead has also been used then the residue will have a red colour. Nitric acid destroys the colour of these pigments. When orange lead is absent, then the colour is destroyed completely and at once, but if it is present, then the colour becomes darker and only disappears on boiling, and lead may be recognised in the solution.

By one or other of the methods given above nearly all the

many varieties of acid and azo dyes can be converted into lakes; there are some, however, which cannot be so used.

The simplest azo compounds are produced by the combination of a base with a phenol or another base; these are insoluble in water, and some of them may be used, especially the combination of para-nitraniline and alpha-naphthylamine with beta-naphthol, in the formation of lake pigments.

The principles underlying their formation are as follows:—Para-nitraniline, $C_6 H_4 N O_2 N H_2$, is dissolved in hydrochloric acid, and this solution is treated with a mixture of sodium nitrite and hydrochloric acid in the cold, when it is converted into diazo-para-nitro-benzene chloride, $C_6 H_4 N O_2 N : N Cl$. This is next brought into combination with the alkaline solution of beta-naphthol, when the diazo compound loses its chlorine atom and combines with the beta-naphthol to form para-nitro-benzene-azo-beta-naphthol—

$$C_6 H_4 N O_2 N : N C_{10} H_6 O H,$$

which has a deep scarlet colour.

In the following is given a detailed method for preparing it on a large scale; by translating the pounds into grammes, and by multiplying the gallons by ten and taking the number obtained as cubic centimetres, the student can make these lakes on a small scale.

From para-nitraniline may be prepared very fine scarlet-red pigment lakes which work well with both oil and water, and keep their colour very well on exposure to light and air. The operations required must be carefully and accurately carried out in order to ensure success. The following method will give the best results:—14 lbs. of para-nitraniline are mixed with 30 lbs. of good hydrochloric acid (it is best to use the pure acid, as the impurities in the commercial grades are liable to affect the brightness of the lake), and 25 gallons of boiling water. This mixture is well stirred until all the para-nitraniline is dissolved; it is then allowed to cool; 25 gallons of cold water are added; and then, slowly and with constant stirring, 10 lbs. of nitrite of soda dissolved in 10 gallons of water are also added. This stage being the most important, special care should be taken to make the solutions quite cold and to mix the ingredients slowly. After about one-half to three-quarters of an hour the preparation will be ready, and there is added 100 lbs. of barytes or other white base, and 30 lbs. of acetate of soda in 25 gallons of water. Next, 14 lbs. of beta-naphthol are dissolved with a little heat in 4 lbs. of caustic soda (77 per cent.) and 25 gallons of water;

this solution is mixed with 25 gallons of cold water, and when the whole is cold, the para-nitraniline solution is added, slowly and with constant stirring, to the preparation of beta-naphthol. The scarlet lake forms at once, and can be filtered, washed, and dried in the usual way, but in drying the temperature must be kept low.

This lake is prepared in fair quantities and sold under such names as Signal Red, Imperial Red, &c.

From alpha-naphthylamine may be prepared in a similar manner a fine crimson-red lake. 14 lbs. of alpha-naphthylamine are gently heated with 30 lbs. of hydrochloric acid and 20 gallons of water until completely dissolved. The solution is then slowly poured into 30 gallons of water. The beta-naphthylamine will be precipitated as hydrochloride in the form of a fine white or faintly-coloured precipitate. This is of no moment provided it be fine and not lumpy in character. The mixture must be allowed to become quite cold before passing on to the next stage. A solution of 10 lbs. of sodium nitrite in 10 gallons of cold water is made, and then poured into the alpha-naphthylamine mixture, the whole being kept constantly stirred for from one-half to three-quarters of an hour, when the operation will be ended. There is next added 30 lbs. of sodium acetate dissolved in 25 gallons of water, and 150 lbs. of barytes. This mass is added slowly to a solution of 14 lbs. of beta-naphthol in 4 lbs. of caustic soda, and 30 gallons of water. The lake forms at once, and is washed, filtered, and dried in the usual manner.

Red Alizarine Lakes.—Method 1.—Weigh out 20 grammes of alizarine and mix with 150 c.c. of water; then add 11 grammes of calcium acetate dissolved in 150 c.c. of water, boil for ten to fifteen minutes, then add 10 grammes of soda crystals dissolved in 150 c.c. of water, in about 10 c.c. at a time. The lake forms fairly quickly; it is filtered off, well washed with the water, and dried as usual.

Alizarine is a type of what are called mordant colouring matters; they enter into combination with the oxides of metals like aluminium, chromium, calcium, and iron, and the compounds so formed are coloured and are called lakes. With true mordant dyes, like alizarine, the colour of the lake will vary with the mordant used; thus, if in place of using alumina sulphate, chrome alum had been used, a very dark red lake would have been got; while if ferrous sulphate had been employed a black violet would have resulted. The student should make these three kinds of alizarine lakes.

In the above method the soda crystals added causes the pre-

cipitation of alumina hydroxide and calcium carbonate by interaction with the alumina sulphate and calcium acetate, and these bodies then enter into combination with the alizarine to form the lake. Instead of forming the alumina hydroxide in the presence of the alizarine, so that its formation and that of the lake goes on simultaneously, it is quite possible to prepare the alumina hydroxide separately and add this to the alizarine to form the lake. But the first method gives the best results.

The method given above yields a pure lake—that is, one containing only the colouring matter and the necessary base with which it is precipitated. Such lakes are excellent and possess strong colouring powers, but are necessarily somewhat expensive. Cheaper lakes are made after the method given below.

Method 2.—Weigh out 50 grammes of barytes, 10 grammes of alizarine, 5 grammes of alumina sulphate, and 2 grammes of acetate of lime; mix with sufficient water, heat slowly to the boil, then add 5 grammes of soda crystals dissolved in water, in small quantities at a time. Finish the lake in the usual way. This gives a cheap lake, but one of inferior staining power.

In place of using barytes, the lake may be diluted by using larger quantities of the alumina sulphate, calcium acetate, and soda crystals by forming a large excess of alumina hydroxide in the lake.

Alizarine Scarlet Lake.—Weigh out 10 grammes of alizarine, 10 grammes of alizarine orange, 10 grammes of alumina sulphate, 2 grammes of tin crystals, 2 grammes of calcium acetate, and 10 grammes of soda crystals, proceeding as described above.

In the same way yellow lakes may be made from alizarine yellow, galloflavine, anthracene yellow, gambine yellow, alizarine azo yellow; orange lakes, from alizarine orange or a mixture of alizarine and one of the above yellows; blue lakes, from alizarine blue, alizarine cyanine, or celestine blue. Chrome alum or chrome acetate is the best precipitant to use for the blues, using much the same proportions of materials as those given under the red lakes. Generally, the alizarine dyes give lakes which, although not brilliant in tint, are very fast to light and air.

CHAPTER VIII.

PAINT OILS AND THINNERS.

PIGMENTS or colours are converted into paint by mixing them in suitable machinery (described in detail in the *Manual on Painters' Colours, Oils, and Varnishes*, Chapter XI.) with a suitable paint oil, generally a mixture of raw and boiled linseed oil in suitable proportions; but inasmuch as such a mixture does not readily lend itself to be spread with a brush on to the surface to be painted, it is necessary to add a proportion of some thinner or more limpid liquid generally known to painters as "thinners." Of these the best known is turpentine or "turps," as it is commonly called, but there is also frequently used coal-tar naphtha, benzol, petroleum spirit or benzoline, shale naphtha, rosin spirit, petroleum or paraffin oil. In the manufacture of oil varnishes from copal, animi, kauri, and similar resins, linseed oil and the liquid solvents above named are used; while for making the so-called spirit varnishes from shellac and sandarac, wood naphtha and methylated spirit are used. The preparation and properties of all these are given in detail in the author's *Manual* just named. Here will be noted such experiments as the student can carry out designed to demonstrate the properties of the paint oils and thinners in use, and to differentiate one from the other.

After which a brief description of each will be given.

All liquid bodies possess some physical properties in common, such, for instance, as specific gravity, contractibility by cold or expansibility by heat, conversion into vapour by heat; while the action of chemical bodies—sulphuric acid, caustic soda, bromine, &c.—varies with different liquids, and is dependent upon the chemical properties of the latter.

SPECIFIC GRAVITY.—It is a matter of common observation that some substances are heavier than others, when equal volumes are compared; thus a gallon of water is heavier than a gallon of linseed oil, and this again is heavier than a gallon of benzoline, while a gallon of mercury is very much heavier than a gallon of water. If one were to take a bottle full of any liquid and weigh it, there would be obtained a series of numbers representing the relative weight of each of these liquids, but

these numbers would only be of interest to the individual observer. As it is a matter of considerable scientific interest to know the relative weights of all bodies, water has been adopted as the standard for liquids and solids; its specific gravity is, therefore, 1·000, and the specific gravity number of a substance, therefore, indicates whether and how much it is heavier or lighter than water. The method of determining the specific gravities of liquids and solid bodies will be dealt with here.

Specific Gravity of Liquids.—There are three convenient methods for ascertaining the specific gravity of oils and liquids—first, by means of the specific gravity bottle; second, by the hydrometer; and third, by the Westphal balance. There are other methods, but for these the student must refer to more advanced manuals on oils.

The *bottle method* of determining the specific gravity method is the most convenient method of determining the specific gravity. The specific gravity bottle is a small thin glass bottle (Fig. 13), fitted with a well-ground glass-stopper which is perforated with a fine tube, so that when the bottle is filled and the stopper inserted it always contains the same volume of liquid. These bottles are made in various sizes to hold 5, 10, 25, 50, or 100 grammes of water. The 25-gramme size is a convenient one, and is well within the capacity of all ordinary chemical balances to weigh. This is used in the following manner:—It is first of all thoroughly cleansed and dried; this is effected by partly filling the bottle with methylated spirit, shaking well, and then pouring the spirit away; next the bottle is partly filled with ether, again shaken, and the ether emptied out.

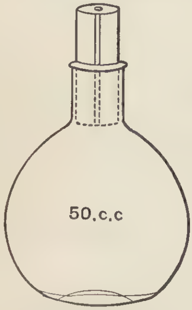


Fig. 13.—Specific gravity bottle.

The bottle is now dried by being placed on an iron plate over the Bunsen burner; when dry it is allowed to cool, and then it is weighed. The sample of oil or liquid to be tested is brought to a temperature of 15° C. (60° F.), and the specific gravity bottle carefully filled with the oil, taking care to avoid air bubbles. The stopper is now gently inserted with a slight twisting movement. Too much pressure is to be avoided, or there is a risk of breaking the neck of the bottle. The bottle must be quite full, without air bubbles under the stopper. The outside of the bottle is wiped quite dry, and the bottle and its contents weighed. Next the bottle is emptied of its contents, cleaned

as before, then filled with distilled water at 60° F., and weighed again. There is now obtained the relative weights of the liquid and water. The weighings should be entered in the note-book of the student in the following manner:—

Specific Gravity of Sample of Linseed Oil.

Weight of bottle + oil, . . .	41·702 grammes.
Weight of bottle, . . .	17·365 ,,
	23·337 ,,
Weight of bottle and water, .	43·363 grammes.
Weight of bottle, . . .	17·365 ,,
	24·998 ,,

From these data the specific gravity is found by dividing the weight of oil by the weight of water, thus—

$$\frac{23{\cdot}337}{24{\cdot}998} = 0{\cdot}9339.$$

It is important to always determine the specific gravity of liquids at 60° F., for heat expands these bodies very considerably, and at 65° F. an oil or other liquid has a very perceptibly lower gravity than at 60° F.; on the other hand, cold increases the gravity. It is found that while different oils have slightly different rates of expansion, yet the differences are so slight that it may be assumed, without much appreciable error, that the specific gravity increases or diminishes 0·00035 for each degree Fahrenheit above or below 60° F.

The Hydrometer Method.—The hydrometer is a glass instrument, shown in Fig. 14, and used by immersing it in the oil contained in a tall cylindrical glass jar after the oil has been brought to the temperature of 60° F. The hydrometer sinks or rises in the liquid in proportion to the specific gravity of the latter, and this is read off on the scale of the instrument at the line which is level with the surface of the liquid.

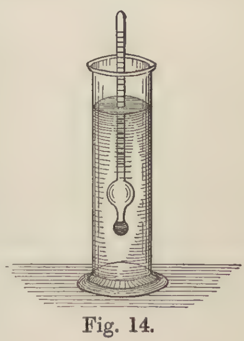


Fig. 14.

No calculations are needed when using the hydrometer. Hydrometers can be had supplied with different scales for the purpose of testing all those oils and thinners used in the paint

trade with something like accuracy. Three will be required; one with a scale from 0·720 to 0·800, one from 0·800 to 0·900, and one from 0·900 to 1·000.

Hydrometers suffer under the disadvantages of requiring a larger volume of oil than is always available, and of many of them being inaccurate owing to faulty construction. The glass jar in which the test is made should not be too small, or the correct gravity will not be obtained.

The *Westphal Balance* is an accurate method of determining specific gravity; it is simple and easy to understand, and gives the gravity direct without any calculations. The principal part of the apparatus is a glass plummet, which has a volume of exactly 3 c.c., and when immersed in water displaces a volume of water weighing 5 grammes. The balance is shown in Fig 15, and consists of a pillar supporting a balance beam, on one end of which the plummet is suspended. The balance is used in the following manner:—The beam is placed upon the stand, and the plummet hung on the end of the beam; this is steadied, and by means of a regulating screw on the base of the instrument a pointer on one end of the beam is brought into a line with a similar pointer on a projecting arm. A glass jar is filled with the oil to be tested, at the standard temperature 60° F., and the plummet dropped in the oil, taking care that it is entirely immersed. With the instrument is provided four riders, weighing respectively 5, 0·5, 0·05, and 0·005 gramme. The largest of these weights is now placed on that division of the beam nearest the plummet, at which it will not depress the balance below the horizontal line; then follow in order of their size the other riders. When the last is in position the specific gravity of the sample has been determined, and it only remains to note the positions of the riders on the beam, in the order of their size, to have the specific gravity of the liquid accurately to the fourth place. Thus, if the 5-gramme rider be at the ninth (9), the 0·5-gramme rider at the third (3), the 0·05-gramme rider at the second (2), and the 0·005-gramme rider at the eighth (8) division on the beam, then the specific gravity is 0·9328. The Westphal balance acts on the principle that when the plummet is immersed in water a weight of 5 grammes is necessary to be

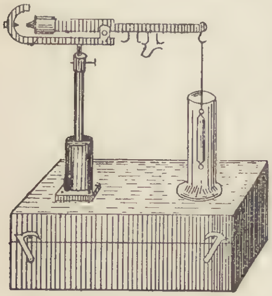


Fig. 15.—Westphal gravity balance.

hung on the hook in order to bring the beam into the hroizontal position again, but in liquids lighter than water a smaller weight is needed according to the specific gravity of the liquid. Now the beam is divided into ten divisions between the central fulcrum on which it turns and the suspension point of the plummet hook; and if the rider be put on the ninth division it exerts only nine-tenths the weight that it does when on the hook, and at the fifth division only five-tenths—that is, one-half its full force; by moving it along the beam we get the first figure in the specific gravity of the liquid. The same remarks apply to the use of the other weights, and it will be noticed that these are respectively one-tenth the weight of the next large one, so that they give in order the succeeding figures in the specific gravity number.

The balance works very well in fairly fluid liquids like water, linseed oil, turpentine, benzene, &c., but does not work well with viscid liquids like glycerine, castor oil, thickened rape oil, &c.

Specific Gravity of Solids—*Powders.*—The specific gravity of pigments, like white lead, barytes, ochre, &c., may be ascertained by the following method, using the specific gravity bottle:—The bottle is cleaned and weighed, a quantity of the pigment is placed in the bottle and the weight again taken, so that the weight of the sample taken is ascertained. A quantity of distilled water is now placed in the bottle, and, after inserting the stopper, it is well shaken, so that the pigment and water get well mixed; it should now be allowed to stand for the pigment to settle down, when the bottle is carefully filled with water, and, after inserting the stopper and drying the outside, the bottle and its contents are weighed. The amount of water in the bottle is thereby ascertained, and this will be less than what the bottle will hold by the volume taken up by the pigment. The weight of the latter divided by the weight of the water, whose space it occupies, gives the specific gravity of the pigment. Thus—

Weight of bottle and pigment, . . .	29·965
„ bottle, ...	17·365
„ pigment, ...	12·600
Weight of bottle, water, and pigment, .	52·521
„ bottle and pigment, . . .	29·965
„ water, ...	22·456

Weight of water bottle will hold, . .	25·000
,, water in bottle, . . .	22·456
	2·544

$$\frac{12·6}{2·544} = 4·55, \text{ the specific gravity of the pigment.}$$

Lumps.—When the solid is in the form of large pieces, such as lump barytes, gypsum, crude ochre, &c., and it is desired to

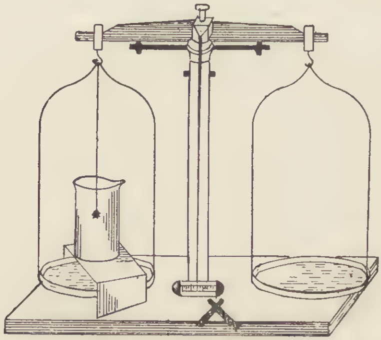


Fig. 16.—Specific gravity of a solid.

determine the specific gravity of these, the arrangement shown in Fig. 16 is very convenient. Across the left-hand pan of the balance is fixed a kind of bridge platform to support a glass beaker. The bridge is made of such a size that the pan swings easily underneath it. By means of a piece of cotton thread the solid whose specific gravity is to be determined is suspended so that it hangs freely in the centre of the beaker. At the same time a similar piece of cotton thread is placed in the right-hand pan of the balance. The weight of the piece is now ascertained in the ordinary way. Then a quantity of distilled water is heated to 60° F. and poured into the beaker until the solid is totally immersed, care being taken that no air bubbles remain adhering to the sides of the solid, or otherwise erroneous results are obtained. The weight of the solid in the water is then ascertained, and this will be less than the weight in the air. By dividing the latter weight by the loss of weight in the water the specific gravity is ascertained.

Thus a piece of crude barytes gave the following figures :—

Weight of barytes in air, . .	12·093	grammes.
,, barytes in water, .	9·464	,,
Loss of weight, . . .	2·629	,,

$$\frac{12 \cdot 093}{2 \cdot 629} = 4 \cdot 59, \text{ the specific gravity of the barytes.}$$

The student will do well to ascertain the specific gravities of linseed oil, rosin oil, mineral oil, maize oil, cotton oil, turpentine, methylated spirit, rosin spirit, coal-tar naphtha, and various pigments by the methods here detailed.

DENSITY OF PIGMENTS.

Closely allied to the specific gravity of pigments is the weight per cubic foot, and in some cases, white lead and zinc white, for instance, it is thought by painters that the higher its weight the better is the pigment. As it is practically impossible for the student to weigh a cubic foot, the best method for him is to have made a little brass box of exactly 1 cubic inch capacity, the tare of which is taken. This box is filled with the pigment, the density of which is to be ascertained, taking care to fill it to its utmost capacity by giving it a few gentle taps with a small hammer or by knocking it on the bench, but not by pressing down the pigment in the box. When filled, the upper surface is levelled by drawing across it a rule or straight edge. The box full of pigment is next weighed. The weight of 1 cubic inch of the pigment is thus got, by multiplying this by 1728 the weight of 1 cubic foot is calculated. If in grammes this may be converted into lbs. by dividing by 453·59, the number of grammes in a pound.

The following figures (weights in grammes) were obtained by the author in this way; they give a good idea of the relative weights of various pigments :—

Chrome yellow, ...	15·31
Rouge, ...	13·12
Ultramarine, ...	12·45
Derby red, ...	40·07
White lead, ...	36·82
Burnt sienna, ...	18·75
Ochre, ...	14·43
Emerald green, ...	36·80
Zinc white, ...	10·95

The white lead weighs 36·82 grammes; multiplying this by

1728 we have 63,724·95 grammes as the weight of a cubic foot; dividing this by 453·59 we get 118 as the weight in lbs. per cubic foot of the white lead.

SAPONIFICATION OF LINSEED OIL.

Weigh out 10 grammes of raw linseed oil in a beaker, add 50 c.c. of alcohol or neutral methylated spirit, and 1 c.c. of an alcoholic solution of phenolphthalein; now drop in from a burette or measuring pipette a decinormal solution of caustic soda, with constant shaking or stirring, until the alcoholic solution acquires a pink tinge which remains permanent for one or two minutes, note the quantity of caustic soda solution required.

This corresponds to the amount of free fatty acid the linseed oil contains, and by multiplying the number of cubic centimetres of soda solution taken by 0·028 the quantity of free linolic acid in the oil is ascertained. This will rarely exceed 3 per cent.

Next weigh out 2 grammes of caustic soda and dissolve in 150 c.c. of water. Add this solution to the oil mixture and heat in a water-bath for about two hours, stirring at short intervals. It will be found that the oil will have disappeared and that a uniform mass of soap liquor is obtained. Next add to this, little by little, with much stirring, some salt until a grainy sort of mass is obtained, consisting of grains of linseed oil-soap floating in a solution of salt. Strain the mass through a piece of clean cloth, running the liquor which comes through into an evaporating basin. The soap which remains on the cloth is carefully removed and put into a beaker.

The liquor or lye, as the soapmaker would call it, in the basin will have a red colour; carefully add hydrochloric acid until this red colour just disappears, and evaporate the whole mass down on a water-bath to dryness. Treat the residue with alcohol, filter from the undissolved salt, and collect the filtrate in a clean porcelain evaporating basin, and evaporate off the alcohol on a water-bath, when a small quantity of a viscid liquid will be left behind; this has a sweetish taste. It is in fact glycerine. Take the soap which has been put in the beaker, add 150 c.c. of water, and boil; the soap will dissolve. Now carefully add a little dilute sulphuric acid, keeping the soap liquor at the boil; an oily layer on the surface of the aqueous liquor will form. Allow the whole to cool, and collect the oil in a separate beaker as completely as possible, and add to it 100 c.c. of alcohol; it will dissolve. Now add 1 c.c. of the

phenolphthalein solution, and run in from the burette or measuring pipette a normal solution of caustic soda until the whole mass acquires a pink colouration. A fairly large quantity of the alkali solution will be needed, thus demonstrating the acid character of the oily layer obtained in this manner from the linseed oil.

In fact, it is really the fat acid of the linseed oil, of which it forms some 94 to 95 per cent. of it; it is not a single acid, but a mixture of several acids whose nature will be more fully discussed presently.

The student is advised to carry out similar experiments with tallow, olive oil, cotton oil, Chinese wood oil, corn oil, palm oil, and cocoanut oil, noting while so doing the colour and appearance of the soap which is formed and of the fatty acids which are got. He will find that all these and any other oil or fat obtained from plants and animals behave in the same way, all yielding glycerine ; hence they are called glycerides ; indeed, it is from such materials that glycerine is obtained. Further, they all yield soap, and hence they are called "saponifiable" oils.

This experiment demonstrates several properties of oils ; in the first place, that they are but slightly soluble in alcohol ; secondly, that they are essentially neutral in character ; any free acid which they contain is really accidental and not essential ; thirdly, that they yield glycerine ; and fourthly, that they yield fatty acids soluble in alcohol.

Glycerine belongs to the group of chemical compounds called alcohols, of which common alcohol is a type ; these bodies possess basic functions, and are capable of uniting with acids to form the group generally known as "ethereal salts." In the oils and fats from vegetables and animals we have glycerine combined with certain acid bodies, varying in nature and number in different oils, which are called the "fatty acids," and of which stearic, palmitic, oleic, linolic, linolenic, ricinoleic acids are examples.

Glycerine is a comparatively weak base ; hence when the oils are boiled with strong bases like caustic soda and caustic potash the oils are decomposed ; the glycerine is eliminated, while the alkali enters into combination with the fatty acid to form soap ; if soda is used as the alkali then what is called a "hard" soap is formed ; while if potash is used then what is known as "soft" soap is the result. This action is called saponification, and is represented in the following equations showing the action of caustic soda and caustic potash respectively on the two typical glycerides, stearin of tallow and linolin of linseed oil :—

$$C_3H_5\begin{cases}C_{18}H_{35}O_2\\C_{18}H_{35}O_2\\C_{18}H_{35}O_2\end{cases} + 3\,Na\,OH = C_3H_5\begin{cases}OH\\OH\\OH\end{cases} + 3\,Na\,C_{18}H_{35}O_2$$

Stearin. Caustic soda. Glycerine. Soap sodium stearate.

$$C_3H_5\begin{cases}C_{18}H_{31}O_2\\C_{18}H_{31}O_2\\C_{18}H_{31}O_2\end{cases} + 3\,K\,O\,H = C_3H_5\begin{cases}OH\\OH\\OH\end{cases} + 3\,K\,C_{18}H_{31}O_2$$

Linolin. Caustic potash. Soap potassium linolate.

The decomposition of the soap by acids is shown in the following equation—

$$K\,C_{18}H_{31}O_2 + H\,Cl = K\,Cl + H\,C_{18}H_{31}O_2$$

Potassium linolate. Hydrochloric acid. Potassium chloride. Linolic acid.

SAPONIFICATION EQUIVALENT.

The experiment given above of boiling linseed oil with caustic soda has shown that oils and the alkali react with one another, but it does not indicate with any degree of accuracy the amount of alkali required to saponify the oil. This can be accurately determined by carrying out what is known as Koettstorfer's saponification test.

Fig. 17.
Oil saponification apparatus.

Koettstorfer's saponification test is one of the most important tests that can be applied to oils, fat oils especially. This is carried out as follows:—Two standard solutions are required, one of caustic potash dissolved in alcohol and containing about 28 grammes of pure $K\,O\,H$ in 1 litre of alcohol. The other is a solution of sulphuric acid containing 24·5 grammes of $H_2\,S\,O_4$ per litre. Both these are what are called by chemists semi-normal solutions. An alcoholic solution of phenolphthalein is used as an indicator, this body is colourless, but alkalies turn it of a deep red colour, while acids destroy this colour. The solution should be rendered of a faint pink tint by adding a drop or two of caustic potash.

Two grammes of the oil or fat are accurately weighed in a flask and 25 c.c. of the alcoholic solution of potash are measured and added. The flask has fitted to it a long glass tube which acts as a condenser (see Fig. 17).

The flask with its condenser tube and contents is heated on a water-bath, the flask being shaken at intervals till the oil is thoroughly saponified, which will take place in about thirty minutes. The flask is then removed, and the contents allowed to cool. A small quantity of the phenolphthalein solution is added, and the standard sulphuric acid run in from a burette, drop by drop, until the red colour of the mixture disappears. 25 c.c. of the potash solution are now boiled in the flask (which has been previously cleaned out) alone for half an hour, and then the contents are titrated with the standard acid as before.

The difference between the two quantities of acid used shows the quantity of potash required to saponify the oil. This difference multiplied by 0·028 gives the weight of KOH in grammes; this multiplied by 100 and divided by the weight of oil gives the weight of KOH (potassium hydroxide) required to saponify 100 parts of oil.

A sample of linseed oil examined in this way gave the following figures:—2 grammes of the oil boiled with 25 c.c. potash and titrated required 6·9 c.c. of semi-normal acid; 25 c.c. of the potash solution by itself required 20·6 c.c. of the acid, so that the oil took a quantity of caustic potash equal to 20·6 less 6·9, or 13·7 c.c. of acid. 13·7 multiplied by 0·028 gives 0·3836 as the quantity of potash required to saponify the 2 grammes of oil, and this multiplied by 100 and divided by 2 gives 19·18, the percentage of KOH required.

Ordinary commercial alcohol or spirit may be used for making the alcoholic solution of potash, provided it be purified by distillation over lime and caustic soda in the following manner:—

The spirit is first placed in a bottle with a small quantity of quicklime and a piece of caustic soda, and allowed to stand for twenty-four hours, being shaken up at intervals. The spirit is next transferred to a retort or flask, and a little fresh lime and soda added. It is then distilled on the water-bath till about 93 per cent. of it has come over; the remaining 5 per cent. is thrown away.

This process frees the spirit from some impurities it contains; these impurities, when acted on by potash, cause the solution to turn dark brown in colour; this colouration interferes somewhat with the operation of titrating with the acid. A slight brownness, however, makes little, if any, difference in this respect, as it disappears, along with the red colour due to the phenolphthalein, at the end of the titration.

The reason for boiling 25 c.c. of the potash alone is because the spirit or alcohol contains impurities which destroy the

potash when boiled with it, and would, therefore, cause the oil to appear to have a higher saponification value; this source of error is eliminated by the method of carrying out a blank test, as described above.

As a rule, oils that resemble olive oil require 19 to 19·5 per cent.; linseed oil takes 18·75 to 19·5 per cent.; solid fats, like tallow, 19·25 to 19·8 per cent.; cocoanut oil, 22 per cent.; butter, 24 per cent.; and sperm oils, 12·3 to 14 per cent. of potash for complete saponification.

A sample of linseed oil which is adulterated with either petroleum oil or rosin oil will absorb proportionately less potash. Thus, a sample of the oil tested in this way took only 17·5 per cent. of potash; now, taking 19 as the mean percentage required by linseed oil, the following calculation,

$$19 : 17{\cdot}5 :: 100,$$

gives 92·1 as the quantity of linseed oil in the sample.

ROSIN OIL.

Weigh a beaker, and into it put 10 grammes of rosin oil; mix it with 50 c.c. of alcohol, add 1 c.c. of phenolphthalein solution, and then slowly run in from a burette normal standard caustic soda until a permanent red colouration is obtained. Note the number of cubic centimetres required. Next add to the mixture caustic soda solution, and boil in a water-bath for one-half to three-quarters of an hour. It will be noticed that, while some action occurs, yet some of the oil is not saponified. Pour the mixture into what is called a separating funnel provided with a tap; put a small quantity of ether into the beaker, rinse it round, and pour it into the separating funnel; repeat this two or three times. Next shake the funnel and its contents well, and then allow to stand for a short time. The contents of the funnel will separate into two layers, one at the bottom, consisting of the water, alkali, and any soap which may have been formed; the upper layer is a mixture of ether with all the unsaponified oil. Open the tap and run out nearly all the lower layer; then put a little warm water into the funnel; shake and then allow to stand; if the upper layer settles out clear, the bottom layer may be run entirely away by a skilful management of the tap; but if the top layer is turbid, then the washing treatment with warm water is repeated. The ether layer is run into a weighed glass beaker, the ether evaporated

off by heating in a water-bath, and, after drying the outside of the beaker, the residual oil is weighed.

This gives the amount of unsaponifiable hydrocarbon oil in the rosin oil.

Rosin oil consists of a complex mixture of acid bodies of unknown composition, the proportion of which is indicated by the volume of normal caustic soda required to neutralise them. There are also bodies which are decomposed by boiling with caustic soda, while there are some hydrocarbon oils which are unattacked by the caustic soda, and are separated from the alkaline products by the treatment with ether. The hydrocarbon oil should be kept for future experiments.

The crude rosin oils contain a large quantity of acid bodies, and, as the process of refining involves the use of caustic soda, it follows that the more refined oils are free from these acid bodies, and approach more nearly to pure hydrocarbon oils in their composition.

MINERAL OR HYDROCARBON OILS.— Place 10 grammes of a lubricating petroleum oil in a beaker, mix with alcohol and phenolphthalein as before, and note that one or two drops of the caustic soda solution is sufficient to produce a permanent pink colouration, thus showing that this oil is free from acid bodies ; next add caustic soda and heat, and it will be observed that the oil is not acted upon. This class of oil consists of a mixture of hydrocarbons which are quite unacted upon by caustic soda or other alkali. Some of the other properties of these oils will be noticed later on, but for a fuller account of them the student is referred to Dr. Boverton Redwood's book on *Petroleum and its Products*, to Alder Wright's *Fats, Oils, and Waxes*, or to Messrs. Archbutt & Deeley's *Lubrication and Lubricants*.

HÜBL'S IODINE TEST.

If an oil is mixed with a small quantity of an alcoholic solution of iodine, the latter gradually becomes decolourised. This has been found to be due to the fatty acid of the oil combining with the iodine and forming compounds with it. The fatty acids present in oils belong to four distinct series. One is the stearic series (better known to chemists as the acetic series). This series of fatty acids does not combine with iodine, so that the larger the proportion of the glycerides of these acids there is in an oil the smaller is the quantity of iodine with which it will combine. The second series of fatty acids is the oleic

series. Each of these is capable of combining with iodine, in the proportion of two atoms of iodine for each molecule of fatty acids. A third series is the tetrolic or linolic series, absorbing four atoms of iodine, and as the acids of this series are characteristic of drying oils, it follows that linseed and other drying oils absorb more iodine than any other class of fatty oils.

Based on these principles is founded Hübl's iodine test, which has for its object the determination of the quantity of iodine absorbed by an oil. It is carried out in the following manner:—Five solutions are prepared—1st, a solution of 25 grammes of iodine in 500 c.c. of alcohol; 2nd, a solution of 30 grammes of mercuric chloride in 500 c.c. of alcohol; 3rd, a solution of 10 grammes of iodide of potassium in 100 c.c. of water; 4th, a solution of 24·8 grammes of sodium thiosulphate (hyposulphite) in 1000 c.c. of water (each c.c. of this is equivalent to 0·0127 gramme of iodine); 5th, a solution of 2 grammes of starch in 100 c.c. of water.

Two grammes of the oil are weighed out and dissolved in 100 c.c. of chloroform; from 10 to 20 c.c. of this solution are taken, and 25 c.c. of the mercury chloride solution and 25 c.c. of the iodine solution are added to it, and the mixture allowed to stand for one and a-half to two hours. The same quantities of the chloroform, iodine, and mercury solutions are also mixed together to make a blank test. At the end of the time 20 c.c. of the iodide solution and 20 c.c. of the starch solution are added, and the mixture titrated with the sodium thiosulphate solution until the blue colour is discharged. The difference in the quantity of the sodium thiosulphate solution used in the two experiments, the blank test and the one with oil, represents the quantity of iodine absorbed by the oil. The quantity of iodine absorbed by 100 parts of oil is called the "iodine equivalent."

Linseed oil absorbs about 150 to 160 per cent. of iodine, while the fatty acids obtainable from it absorb 201 per cent. Next to linseed oil, rape and cotton-seed oils absorb the most (about 100 per cent.). The following table gives some information on this iodine absorption of oils:—

Linoleic acid, ...	201·5 per cent.
Linseed oil, ...	158 ,,
Cotton oil, ...	106 ,,
Rape oil, ...	100 ,,
Oleic acid, ...	89·8 ,,
Ricinoleic acid, . . .	85·0 ,,
Castor oil, ...	84·4 ,,
Olive oil, ...	82·8 ,,
Cocoanut oil, ...	8·4 ,,

Mineral or petroleum oils absorb iodine to a small extent (about 8 per cent.), while rosin oils are very variable, taking up from 10 to 50 per cent.

The oil chemist will probably find the bromine absorption test, devised by Hehner and described below, rather more convenient to use, for it is more certain in its action than the Hübl test, and is much more easily carried out.

HEHNER'S BROMINE TEST.

Mr. O. H. Hehner described (*Analyst*, 1895, p. 50) the following gravimetric method of determining the bromine absorption of oils. A small wide-mouthed flask is carefully weighed, and from 1 to 3 grammes of fat introduced into it. This is dissolved in 10 c.c. of chloroform, and then pure bromine is added drop by drop until the bromine is decidedly in excess. Both the chloroform and the bromine must be previously tested in a blank experiment, to make sure that they leave no appreciable residue on heating. The flask and its contents are then heated on the water-bath till most of the bromine is driven off, a little more chloroform is added, and the mixture again heated, the chloroform vapour helping to drive out the excess of bromine. The flask and its contents are placed in the air-bath, regulated for about 125° F., and kept there until repeated weighings show their weight to be constant; this takes several hours. Some acrolein and hydrobromic acid escape during the drying. The increase in weight is the weight of the bromine absorbed. This process gives very satisfactory results. The writer has obtained the following figures from different oils:—

Menhaden fish oil, . . .	43·6	per cent.
Pale seal oil, ...	87·6	,,
Pale whale oil, ...	4·6	,,
Scotch cod oil, ...	59·9	,,
Japan fish oil, ...	123·3	,,
Arctic sperm oil, . . .	59·9	,,
Straw seal oil, ...	137·2	,,
Olive oil, ...	51·3	,,
Lard, ...	40·6	,,
Butter, ...	21·6	,,
Castor oil, ...	43·7	,,
Linseed oil (raw), . . .	114·2	,,
Linseed oil (boiled), . . .	112·0	,,

THE FLASH POINTS.

The oils and spirits used in painting are inflammable substances; benzoline, shale naphtha, coal-tar naphtha, and methylated spirit are inflammable at ordinary temperatures, and immediately take fire when a flame is brought into contact with them; on this account considerable care should be taken when handling or working with these bodies to prevent them or their vapour from coming into contact with a light. Turpentine, rosin spirit, and petroleum oil take fire only when heated to temperatures varying from 100° to 150° F.; while rosin oil requires heating to about 350° F., and linseed oil to 600° F. before they will take fire. When experiments are made with a view of ascertaining the firing point or fire test of an oil, &c., it is found that prior to the temperature reaching the point at which the oil, &c., will burn, there is an intermediate point at which scintillations of flame appear, this is called the "flash point," and this, like the firing point, varies with different oils and thinners, and in some cases, as in the adulteration of linseed oil with rosin oil or mineral oil, or the adulteration of turpentine with coal-tar naphtha, or low grade petroleum oils, forms a valuable means of testing the oils.

The simplest and easiest way of carrying out the flash-point test is the following:—Provide a small copper test cup or porcelain crucible capable of holding $1\frac{1}{2}$ ozs. of the oil to be tested. If such oils as linseed or rosin oil, which have high flash points, are to be tested, this vessel may be supported on an iron plate over a Bunsen burner; but if turpentine or petroleum oils, which flash at about 100° to 150° F., are to be tested, then the cup should be placed in a bath of water. The cup should be filled about three-fourths full of the sample to be tested, and in the centre of the oil is suspended a thermometer. Heat is applied, not too strongly, so that the heat does not rise more than 5° to 10° per minute. A blowpipe is now connected with a gas tap and a small jet of flame, about the size of a small pea, lit at the end. Frequently, as the temperature of the oil rises, this jet of flame is brought near to, but should not touch, the surface of the heated oil, &c.

Presently a small blue flame will flash across the surface of the oil, and almost as speedily disappear. The temperature at which this happens is called the "flash point," and should be noted.

Continuing the experiment, it will be observed that the flashes come at more frequent intervals and become more luminous,

until at last the oil takes fire and burns continuously; the temperature at which this occurs is called the "fire test" or "burning point." When it occurs the heating should be stopped and the thermometer withdrawn from the burning oil, and a small tin plate or cover placed over the cup, by which means the flame of the burning oil will be extinguished.

Fig 18 shows the arrangement for carrying out this experiment for the determination of the flash point. This arrangement is fairly satisfactory for the majority of oils, especially for those which, like linseed oil, flash at high temperatures, and by exercising due care very good results are obtainable. It is necessary that the heating of the oil should not be too rapid, that the experiment be carried out where there are no draughts, and that the small testing gas jet should not be held too long above the oil or in contact with it. A momentary immersion into the space above the oil is all that is needed.

For the testing of petroleum oils, turpentine, rosin spirit, and all liquids which flash from, say, 150° F. downward, the Abel flash point apparatus shown in Fig. 19 is the best.

The student should make experiments on the flash and fire tests of linseed oil, rosin oil, turpentine, and all such bodies as are used in paint- and varnish-making, and while doing so should notice any minute differences which show themselves in the manner in which the oils flash and burn, as such differences will often enable him to detect adulteration in oils and thinners.

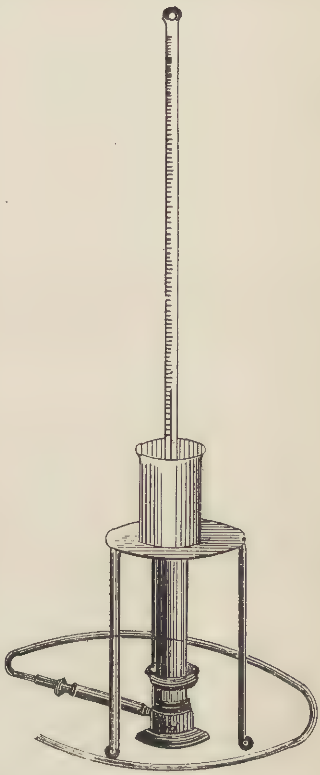


Fig. 18.—Flash point apparatus.

Generally speaking, linseed and other fatty oils flash at about 500° F., sometimes a little below, at other times above, depending

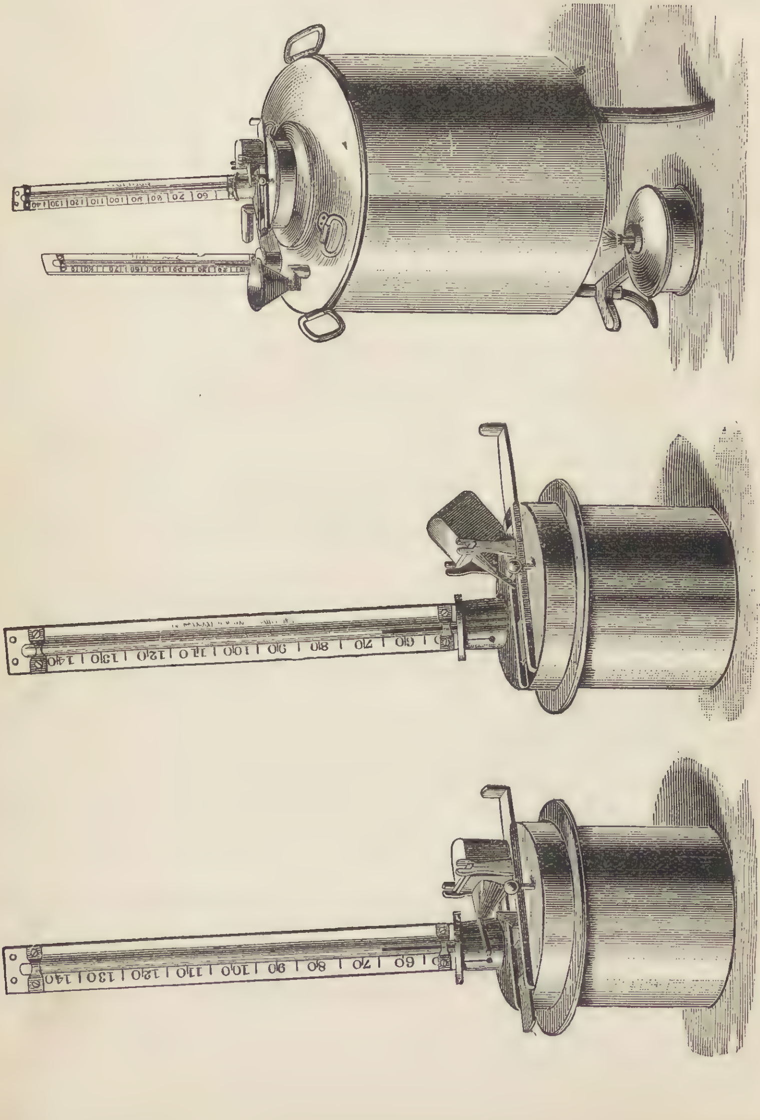


Fig. 19.—Abel's flash point apparatus.

on the quality of the sample under test. Mineral oils, such as are now largely used for lubricating ordinary machinery, flash at from 375° to 420° F.; this latter being the highest flash point known for these. The class of oils specially made for lubricating steam engine cylinders flash at from 450° to 540° F., but such oils are not used in the paint trade. Rosin oil flashes at from 310° to 320° F., and with a peculiar scintillating flame. Turpentine and rosin spirit flash at from 96° to 98° F., petroleum burning oils at from 73° to 110° F., paraffin burning oils at from 100° to 120° F., methylated spirit at 57° F., benzoline, shale naphtha, and coal-tar naphtha at much lower temperatures. These figures must be taken as a guide, not as the absolute flash points of the oils, &c., enumerated.

For further information regarding various methods of determining the flash point of oils, reference can be made to Dr. Boverton Redwood's *Petroleum* and to Messrs. Archbutt & Deeley's *Lubrication and Lubricants.*

PAINT OILS.

The various fatty oils which are derived from vegetables and animals may be roughly divided into three divisions—

1st. Non-drying oils.
2nd. Semi-drying oils.
3rd. Drying oils.

The non-drying oils comprise such oils as olive oil, sperm oil, whale oil, cocoanut oil, lard oil, &c., which, on exposure to the air, either remain unchanged or, at the most, become slightly more viscid. Such oils are of no use in painting, although this very property causes them to be of value in the lubrication of machinery.

The semi-drying oils comprise a few, such as cotton-seed oil and corn oil, which, when exposed to the air, tend to become more viscid and gummy in appearance, but never dry quite hard. These oils are not suitable for the lubrication of machinery nor for paint-making, but are much used for soap-making and for food. From time to time such oils are offered to painters, either as paint oils pure and simple, or to be added to paint, but their use for this purpose is most unsatisfactory, and painters would be well advised to give them a wide berth.

The drying oils are those which, like linseed, poppy-seed, and Chinese wood oils, when exposed to the air, especially in thin

films, are found to absorb oxygen from it and become changed to a hard firm mass; they are said to "dry." This is the property which gives them value for making paint, but is an absolute bar to their use for the lubrication of machinery.

These oils will now be briefly described. For a longer account reference can be made to the author's *Manual.*

CHEMISTRY OF OILS.—The experiment made by boiling up linseed oil with caustic soda will have shown the student that oils are a combination of glycerine with various acid bodies, which are denominated the fatty acids, and of which a large number are known. The following remarks on these bodies are taken from the writer's *Painters' Colours, Oils, and Varnishes.*

The oils belong, chemically, to that group of bodies known as salts, which may be defined as compounds containing two radicles, one of which is of acid origin, the other of basic origin.

In the case of oils the latter is always the body known as glyceryl, $C_3 H_5$, which, when combined with hydroxyl, $H O$, forms the well-known compound glycerine, $C_3 H_5 (H O)_3$; hence oils are frequently known as glycerides, because on saponification they yield glycerine. In the oils this glyceryl is united with various acids; for, while there is only one base present in any oil, there are rarely fewer than two acids present, and often there are many more. These acids are known as fatty acids, and form a numerous group, or rather several groups of bodies. Some of these, such as oleic, stearic, palmitic, and linolic are found present to a greater or less extent in all oils; others, such as arachidic, ricinoleic, valeric, &c., are only found in small quantities, and often only in certain oils of which they are the characteristic constituent, such as ricinoleic acid in castor oil, arachidic acid in ground nut oil, valeric acid in fish oils, rapic acid in rape oil, linolic acid in linseed oil, and so on.

The fatty acids may be divided into five groups, which, from the most prominent acid they contain, may be named, 1st, the stearic acids; 2nd, the oleic acids; 3rd, the linolic acids; 4th, the linolenic acids; and 5th, the ricinoleic acids.

The first group is a very numerous and important series of acids, and is often called, from the most important member of the series, the acetic acid group. Many of these bodies, such as acetic acid and stearic acids, are used on a large scale in various industrial operations; others are of importance as occurring in products which are of good industrial value. The following lists comprise the best known members of each series :—

1. STEARIC SERIES OF FAT ACIDS.

Name.	Formula.	Name.	Formula.
Formic, . .	$H\,C\,H\,O_2$	Myristic, . .	$H\,C_{14}\,H_{27}\,O_2$
Acetic, . . .	$H\,C_2\,H_3\,O_2$	Pentadecatoic, .	$H\,C_{15}\,H_{29}\,O_2$
Propionic, . .	$H\,C_3\,H_5\,O_2$	Palmitic, . .	$H\,C_{16}\,H_{31}\,O_2$
Butyric, . .	$H\,C_4\,H_7\,O_2$	Margaric, . .	$H\,C_{17}\,H_{33}\,O_2$
Caproic, . .	$H\,C_6\,H_{11}\,O_2$	Stearic, . .	$H\,C_{18}\,H_{35}\,O_2$
Œnanthylic, . .	$H\,C_7\,H_{13}\,O_2$	Arachidic, . .	$H\,C_{20}\,H_{39}\,O_2$
Caprylic, . .	$H\,C_8\,H_{15}\,O_2$	Medullic, . .	$H\,C_{21}\,H_{41}\,O_2$
Pelargonic, . .	$H\,C_9\,H_{17}\,O_2$	Behenic, . .	$H\,C_{22}\,H_{43}\,O_2$
Capric, . . .	$H\,C_{10}\,H_{19}\,O_2$	Lignoceric, . .	$H\,C_{24}\,H_{47}\,O_2$
Cocinic, . .	$H\,C_{11}\,H_{21}\,O_2$	Geoceric, . .	$H\,C_{26}\,H_{51}\,O_2$
Lauric, . . .	$H\,C_{12}\,H_{23}\,O_2$	Cerotic, . .	$H\,C_{27}\,H_{53}\,O_2$
Tridecatoic, . .	$H\,C_{13}\,H_{25}\,O_2$	Melissic, . .	$H\,C_{30}\,H_{59}\,O_2$

Formic and acetic acids are liquids having a powerful acid odour, are soluble in water, and can be distilled without change. The next few members of the series are liquids more or less soluble in water, and can be distilled without any change; they have a slight odour of rancid fat, and are known as the soluble fat acids, being present in such fats as butter, cocoanut oil, and palmnut oil, and are occasionally found present in small quantities in fish oils. The higher members of the series, or from capric acid upwards, are solids; they are insoluble in water, and cannot, as a rule, be distilled without being decomposed.

The fat acids are soluble in alcohol, ether, turpentine, and similar solvents; they are monobasic acids combining with one equivalent of potassium hydroxide (caustic potash) or sodium hydroxide (caustic soda) to form soaps, which are more or less soluble in water, the salts of the lower fatty acids being freely soluble, while those of the higher acids are rather difficultly soluble, the solubility decreasing with the complexity of the fatty acids.

2. OLEIC SERIES OF FATTY ACIDS.

Name.	Formula.	Name.	Formula.
Acrylic, . .	$H\,C_3\,H_3\,O_2$	Physetoleic, . .	$H\,C_{16}\,H_{29}\,O_2$
Crotonic, . .	$H\,C_4\,H_5\,O_2$	Hypogæic, . .	$H\,C_{16}\,H_{29}\,O_2$
Angelic, . .	$H\,C_5\,H_7\,O_2$	Gæidic, . .	$H\,C_{16}\,H_{29}\,O_2$
Pyroterebic, .	$H\,C_6\,H_9\,O_2$	Oleic, . . .	$H\,C_{18}\,H_{33}\,O_2$
Damaluric, . .	$H\,C_7\,H_{11}\,O_2$	Elaidic, . .	$H\,C_{18}\,H_{33}\,O_2$
Damolic, . .	$H\,C_{13}\,H_{23}\,O_2$	Doeglic, . .	$H\,C_{19}\,H_{35}\,O_2$
Moringic, . .	$H\,C_{15}\,H_{27}\,O_2$	Brassic, . .	$H\,C_{22}\,H_{41}\,O_2$
Cimicic, . .	$H\,C_{15}\,H_{27}\,O_2$	Erucic, . .	$H\,C_{22}\,H_{41}\,O_2$

These acids are very characteristic of fats and oils. Oleic is by far the commonest of all fat acids, as when combined with glyceryl it forms olein, the fluid constituent of almost all oils.

The lower members are more or less soluble in water, and volatile by heat without decomposition; the higher members are insoluble, and are decomposed by heat.

3. LINOLIC SERIES OF FATTY ACIDS.

Name.	Formula.
Elæomargaric, ...	$H C_{17} H_{29} O_2$
Linolic, ...	$H C_{18} H_{31} O_2$
Tariric, ...	$H C_{18} H_{31} O_2$
Millet oil acid, ...	$H C_{18} H_{31} O_2$

4. LINOLENIC SERIES OF FATTY ACIDS.

Name.	Formula.
Linolenic, ...	$H C_{18} H_{29} O_2$
Isolinolenic, ...	$H C_{18} H_{29} O_2$
Jecoric, ...	$H C_{18} H_{29} O_2$

5. RICINOLEIC SERIES OF FATTY ACIDS.

Name.	Formula.
Ricinoleic, ...	$H C_{18} H_{32} O H O_2$
Ricinisoleic, ...	$H C_{18} H_{32} O H O_2$
Rapic, ...	$H C_{18} H_{32} O H O_2$

Linolic and linolenic acids are characteristic of linseed and other drying oils, while ricinoleic acid, which has properties very different from other acids, is found only in castor oil.

Both the oleic and linolic series of acids are monobasic, like the stearic series, and combine with potash and soda to form soaps which are rather more soluble in water than the soaps made from the stearic acids.

The ricinoleic series of acids are hydroxy acids containing one hydroxyl (O H) group in their molecule, their constitution being represented by the formula—

$$\left\{ \begin{array}{l} C_{17} H_{31} O H \\ C O O H. \end{array} \right.$$

They are monobasic acids, combining with one equivalent (Na O H) of caustic soda; they differ from all the other fatty acids in being insoluble in petroleum ether, a property which extends to their glycerides, and in yielding alkali soaps, which are more freely soluble in water than the soaps of most other fatty acids.

DRYING OILS.

The following is a fairly complete list of the drying oils at present known :—Linseed, lallemantia, hempseed, walnut, poppy

seed, sunflower, Chinese wood oil, fir seed, madia, candle nut, tobacco seed, and weld seed. Of these linseed is by far the best and the one mostly used for this purpose. Chinese wood oil has been offered in increasing quantities of late; poppy-seed and walnut oils are sometimes used by artists on account of their light colour; hempseed oil is not much used in this country, but in Russia is largely used; the other oils are of only slight interest. Another oil often used in America is Menhaden oil from the Menhaden fish found on the Atlantic coasts of the United States.

LINSEED OIL.

This important drying oil is obtained by pressing the seeds of the flax plant, *Linum usitatissimum*, a plant which grows in many places in the temperate zone, and which is extensively cultivated in Ireland, Belgium, Holland, America, Russia, India, and other countries for the sake of its fibre and its seed. The fibre is used in the manufacture of linen cloth, while the seed oil is used in medicine and for expressing linseed oil.

EXTRACTION OF LINSEED OIL.—In order to obtain the oil from the seed the latter is passed through several operations. It is first cleaned to free it from dirt and, as far as possible, from other seeds. Next the seed is crushed by passing it through a roll mill or under edge-runners; the crushed seed is next heated in a kettle, with the object of coagulating the albuminous matter of the seed and at the same time rendering the oil more fluid, so that it will flow more freely from the seed when pressed.

The hot seed is then made up into cakes and put under the plates of an hydraulic press specially constructed for the purpose; here it is subjected to a pressure of about 750 lbs. per square inch for a few minutes, followed by a pressure of 2 tons for a short period.

Each of the operations above noted takes about twenty minutes. The yield of oil varies with different varieties of linseed, and also in the same seed, according to the climate prevailing during the year in which it was grown; approximately it may be put at 30 per cent. of the weight of the seed.

The linseed oil flows from the presses into suitable storage tanks. This crude oil contains—

1. The glycerides of the linseed oil acids.
2. Water.
3. Mucilage, albumen, &c.

4. Colouring matters of the chlorophyll group, not in large quantity, varying in oils from different localities, and imparting varying shades of brown, green, &c., to the oil.

Of all these bodies only the first named are of any value to the painter; and in order to remove the others the oil is subjected to a refining process, the character and extent of which varies with different oil refiners.

It is not desirable to subject the oil to any very energetic operation, for such treatment can and does only lead to deterioration of the oil for use as a paint oil.

In some cases all that is done is to run the oil into a tall tank placed in a warm place, or in which a steam coil is fixed, so that the oil may be warmed. The temperature should be about 100° to 110° F.; in these tanks it is allowed to stand for from three to six months, when all the moisture, mucilaginous and albuminous matter settles out, leaving the oil at the top perfectly clear and transparent, but possibly highly coloured. This process suffers from being slow and producing a comparatively large quantity of sedimentary matter technically called "foots," so that it is not often adopted, but for those oils which are to be used for making varnishes no better process can be adopted.

The oil foots can be used in making putty or soft soap.

Another process of refining the oil consists in placing the oil in large lead-lined vats and heating it with a steam coil to about 150° F., in order to coagulate the albumen; the oil may be allowed to stand to clarify, or may be dealt with more speedily by sending it through a filter press into another vat; here it is treated with 3 lbs. of sulphuric acid for each 112 lbs. of oil, the acid being mixed with an equal volume of water. The oil and acid are thoroughly mixed, which is best done by blowing a current of air through the mass; after which the oil mixture is allowed to stand, when the acid collects at the bottom, leaving the clear oil at the top. This acid layer is run off and clean warm water thoroughly mixed with the oil to wash out any traces of acid from it. The oil and water should be allowed to stand for some time in a warm place so that the water can settle out completely from the oil. The acid acts upon and destroys the albuminous and colouring matters present in the oil, and oil refined in this way is usually paler than oil which has been clarified by standing.

COMPOSITION AND PROPERTIES OF LINSEED OIL.—Linseed oil is sold to painters in two forms known as "raw" and "boiled" oil. Raw linseed oil is the oil as it comes from the presses or such refining processes as have been noted

above. What is sometimes sold as refined linseed oil is simply raw oil rather better refined and bleached by exposure to sunlight, also, sometimes, a little litharge or acetate of lead is mixed with the oil before subjecting it to the bleaching process.

Raw linseed oil is a yellowish coloured oil having a more or less brownish colour; it possesses a peculiar characteristic odour and taste, which serves to distinguish it from other oils. It is clean and limpid at all ordinary temperatures; when subjected to a cold equal to $-27°$ C. it solidifies.

The locality from whence the seed comes has an important influence on the quality of the oil; the best is that pressed from Baltic seed, and this is largely used in the preparation of varnishes. Black Sea seed also yields a good quality of oil. A large quantity of oil is pressed from East India seed, but this is not so good as the other oils; it is largely used in the manufacture of printing inks. Other varieties of the oil are also known.

The specific gravity of linseed oil averages 0·935 at 60° F.; it is rarely lighter than 0·932, or heavier than 0·937; it is not constant even in the same variety of oil. Baltic oil is usually heavier than other varieties. At 212° F. the oil has a gravity of about 0·880.

Linseed oil is soluble in about forty times its volume of alcohol at the ordinary temperature, or in about five times its volume at 180° F. It is soluble in glacial acetic acid at 180° F. It is readily soluble in such solvents as ether, petroleum spirit, shale naphtha, turpentine, and chloroform.

In connection with the foregoing facts the student is advised to obtain samples of various qualities of linseed oil, and find their specific gravities by the methods given on pp. 166-168; and also to test their solubility in the various solvents just named.

Sulphuric acid has a strong action on linseed oil, causing it to become thick and of a dark colour; large quantities of sulphur dioxide are evolved, while the temperature of the mixture is considerably increased, the amount varying somewhat in different kinds of linseed oil. Thus, with Baltic linseed oil, the author obtained an increase of 120° C., with Black Sea oil an increase of 114° C., and with East Indian oil an increase of 106° C.

The action of nitric acid varies with the strength of the acid; a moderately strong acid converts linseed oil into a viscid yellowish mass, which is insoluble, or nearly so, in petroleum spirit or benzol; while strong, fuming nitric acid often causes linseed oil to take fire. Nitrous acid does not give a solid elaidin with linseed oil.

In glacial acetic acid it is readily soluble on warming, while the turbidity temperature ranges from 36° C. to 47° C., according to the quality of the oil and the strength of the acetic acid.

Linseed oil combines very readily with bromine and iodine, absorbing a larger proportion of these bodies than any other oil; there are slight differences between the various kinds of linseed oil in the quantities of iodine and bromine that they will combine with, but it may be laid down as a rule that the better the quality of the oil, the more iodine or bromine will it absorb. The average absorption of iodine is 156 per cent. of the oil, while of bromine the average is 98 per cent. That is, 100 parts of linseed oil will combine with 156 parts of iodine, or with 98 parts of bromine.

The property which gives linseed oil its special value as a paint oil is that when exposed to the air it gradually absorbs a large proportion of oxygen, forming a new compound of a resinous character, the properties of which have never been fully investigated. In this power of combining with oxygen, linseed is distinguished very remarkably from other oils, which have little or no power of combining with oxygen. W. Fox gives the following as the number of cubic centimetres of oxygen absorbed by 1 gramme of various oils:—

Baltic linseed oil,	191
Black Sea linseed oil,	186
American linseed oil,	155
East Indian Bombay oil,	130
East Indian Calcutta oil,	126
Cotton-seed oil,	24·6
Brown rape oil,	20
Colza oil,	17·6
Olive oil,	8·2

Evidently the quality of linseed oil depends very much upon its oxygen-absorbing powers; thus, Baltic oil, which dries better than any other variety of linseed oil, takes up more oxygen than Black Sea or East Indian, which latter takes up the least, and is not equal to Black Sea oil in its drying properties, but it is much better than East Indian, owing, as is clear, to its greater absorbing power for oxygen.

BOILED OIL.

The drying power of linseed oil may be increased by the process known as "boiling" it. There are in use now three methods of preparing boiled, or so-called boiled, oils—fire boiling, steam boiling, and a cold process.

The student may experiment with all these three processes.

FIRE BOILING.—Place a tall narrow beaker on a tin plate over the Bunsen burner, and in it put 100 grammes of oil; apply heat and raise the temperature to 300° F., at which it is maintained for half an hour; now add 2 grammes of finely-powdered acetate of lead, and mix it thoroughly with the oil; raise the temperature to 400° or 420° F., and maintain at that heat for one hour, when the oil may be allowed to cool down. When cold, its condition may be observed, its specific gravity determined, and its drying power tested by spreading out a little on a clean glass plate and exposing it to the air, best over night. If circumstances permit, it would be a good plan to start with a larger quantity, say 500 grammes, of the oil, heating for one hour at 300° F., then adding 10 grammes of lead acetate and keeping the oil at 400° to 450° F. for five to six hours, taking out about 50 grammes at intervals, for the purpose of watching the effect continued heat has on the colour, gravity, and drying power of the oil. It will be observed that these increase as the duration of heating increases.

Experiments on similar lines may be carried out by replacing the acetate of lead by litharge, red lead, manganese oxide, manganese borate, manganese sulphate, resinate of lead, or resinate of manganese. These bodies are called "driers"; they will be described more fully later on, as they have an important influence on the drying power of the oil.

In experimenting with these the quantity added to the oil should be noted, and the effect on the colour, rapidity of drying, and character of the film left observed.

On the large scale, oil is boiled in iron pans, varying in size, according to the requirements of the oil boiler, from 100 to 600 gallons. These are built into suitable furnaces, the fire of which can be fed from the outside of the building, so that if the oil should boil over, as it may sometimes do, it will not find its way to the fire. A hood ought to be placed over the pan to carry away vapours from the oil, for these are of an acrid character and unpleasant to the workmen. The process is as follows:—The oil is placed in the boiler, which should never be more than two-thirds full, and the fire lighted. While the temperature of the oil is rising, the fluid should be closely watched, as it is then that effervescence is likely to take place, and the oil to boil over with possibly disastrous results. Should there be any sign of the oil boiling over to too great an extent, the fires should be withdrawn, and, by beating the oil, or ladling it out into another boiler, efforts should be made to keep down the effervescence.

Much of this is due to the presence of small quantities of water in fresh-pressed oil; oil which has been kept for some time after pressing has less, since in it the water and mucilaginous matter have had a chance of settling out. After some time, dependent upon the quantity of oil being treated, the heat is raised to the "boiling point." This is usually at a temperature of about 500° F. The heating of the oil to this temperature should not be too rapid, so as to give the oil every chance of becoming oxidised, and it should not take less than two hours; a longer time is preferable.

When the oil has reached the boil, or, better, after it has been boiling for about half an hour, a small quantity of driers is added; other additions of the same are made at short intervals during a period of three hours. The total amount of driers added varies a little in different works, but it averages about 5 lbs. to 1 ton of oil. After all the driers have been added, the oil is boiled for one hour longer; then the fire is drawn, and the oil allowed to stand over night to cool and settle. The clear oil at the top is sent into the warehouse and sold as "boiled oil," while the turbid oil at the bottom is known as "boiled oil foots," and is used in making putty or putting into cheap ready mixed paints. It is not advisable to add the whole of the driers at once, small as it is in proportion to the oil, as the action between the two might become too great, and the oil enter into rather violent ebullition, which could not be controlled readily; by adding small quantities at a time the action between the driers and the oil is less energetic and the boiling more under control; besides that, the combination between the driers and the oil is more complete.

During the process of boiling the oil undergoes some decomposition. Water is continually being given off, while large quantities of acrolein, C_3H_4O (a derivative of glycerine, which has a powerful action on the lachrymal glands), acetic acid, formic acid, and other acids are also given off. As these products are somewhat obnoxious to the workmen, they should be conveyed by means of a collecting hood into the chimney of the works. The oil acquires a dark red colour, due to the presence of some of the products of the decomposition of the oil, although much depends upon the temperature at which the boiling is done. If this be kept below 400° F., a comparatively pale oil is produced; while if it be above 500° F., then a dark coloured oil is sure to result. The demand is for a pale oil, so that in boiling it is desirable to keep the temperature as low as possible. The quantity and nature of the driers used have some influence on

the colour of the oil. Manganese produces a darker oil than any other drier; next to this are red lead and litharge. The acetates of lead and manganese, and the oxalate of the latter metal, produce the palest oils.

It will be found best to give an hour's extra boil at a low temperature, say from 400° to 450° F., rather than to heat the oil to 500° F. and over, when darkening is sure to occur.

What the character of the action is which goes on during the process of boiling linseed oil is somewhat uncertain. That oxidation occurs is certain, but that is all that is definitely known; probably linoxyn, which may be regarded as the resin of linseed oil, is formed to some extent. Then when driers are used there is formed a combination of linolic acid with the base of the driers, which, dissolving in the rest of the oil, forms a kind of varnish, to which action some of the gloss of boiled oil is due.

STEAM BOILING PROCESS.—In this process steam heat is used, so that the operation is less risky to carry out, while the oil is paler in colour. A jacketted or double-cased pan is provided, and in the space between the outer and inner pan steam is sent. In the oil-pan agitators are provided, so as to thoroughly mix the oil and any driers used, while a current of air is blown through the oil at the same time. The method of working is to heat the oil for, say, two hours at about 210° F., stirring well all the time; then the driers are added in small quantities at a time, the heating is kept up and at the same time the air is sent in, the whole operation taking from six to eight hours. The amount of driers added varies from $\frac{1}{2}$ lb. to 1 lb. to each cwt. of oil. The steam process produces a paler oil than the fire process, and one which yields a more elastic coat.

The Blenkinsop-Hartley process of preparing a drying or siccative oil consists in the following operations:—1. The oil is treated with a mixture of 3 volumes of water to 1 of strong sulphuric acid, the two bodies being well mixed together and then allowed to stand for two or three days. 2. The pale and clear oil is next mixed with a solution of manganese linoleate in turpentine. 3. The oil is heated to 212° F. in a special apparatus, and air blown through the oil for a sufficient length of time to produce an oil of suitable specific gravity.

The drying or siccative oil obtained by this process is very pale in colour, paler even than raw oil, and has a specific gravity of from 0·940 to 0·947. It is an excellent oil, and for mixing with pale coloured pigments it is superior to fire boiled oil.

Ozone, or more strictly ozonised air, has been used in preparing drying or siccative oils.

The raw linseed oil is first mixed with a solution of manganese linoleate in turpentine, and then the oil is sprayed into a chamber filled with ozone, this spraying being repeated several times, when a quick-drying oil is obtained which is paler in colour than raw linseed oil, and dries with a more elastic coat than ordinary boiled oil.

So-called "boiled oils" are now frequently made by dissolving 1 to 1½ lbs. of manganese resinate or of manganese linoleate in 1 gallon of raw linseed oil by heat, then mixing this with 20 gallons of raw linseed oil heated to 200° F. The result is not satisfactory. The product has very little more drying power than raw linseed oil, and dries with but little more gloss.

PROPERTIES OF BOILED OIL.—As ordinarily prepared, boiled oil is a slightly viscid oil of a reddish colour, varying a little in depth of colour according to the temperature, and the length of time it has been heated in the process of boiling. Its odour is peculiar, and its specific gravity varies a good deal, but the average is about 0·945; some samples will reach 0·950, while others may be as low as 0·940. Boiled oil is soluble in turpentine, petroleum spirit, shale spirit, benzene, carbon bisulphide, and other similar solvents. When boiled with caustic soda or caustic potash it is saponified almost completely; there is usually a small trace of unsaponifiable hydrocarbon oil formed by the decomposition of the oil during the process of boiling.

When exposed to the air in thin layers it dries much more rapidly than raw linseed oil, and leaves behind a hard, lustrous coat; it is this property which makes boiled oil of so much use to the painter; yet it does not do to use boiled oil alone in the making of paints, because the coat which it leaves is too hard and rather liable to crack on exposure to the air; raw linseed oil is always added, as, by leaving a more elastic coat, it prevents this bad fault of boiled oil from showing itself.

ADULTERATION OF LINSEED OIL.—Both the raw and boiled linseed oils are frequently adulterated. The principal adulterants used are mineral and rosin oils. Other fatty oils, such as cotton-seed, niger-seed, and whale oils are sometimes used, but, as linseed oil is cheap, the small gain arising from their use does not compensate for the probable loss of custom which must ensue if the adulteration be found out, while the great difference in the cost of linseed and mineral oils is a strong inducement for adulterating with the latter.

For the purpose of detecting adulteration the following tests may be applied :—

Specific Gravity.—For raw linseed oil this should be about 0·932; if less than 0·930, adulteration with fish, seed, or mineral oils would be indicated, while, if the specific gravity exceeds 0·937, there has very likely been admixture with rosin oil. The specific gravity of boiled oil averages about 0·945; if much heavier than this it is quite probable that rosin oil has been mixed with the oil, while if below 0·940, then other fatty and mineral oils may be looked for.

Flash Point.—Linseed oil, whether raw or boiled, flashes at 500° F. Other fatty oils flash at about the same temperature. Rosin oil flashes at from 300° to 330° F., and during the process of testing a strong odour of rosin would be given off. Mineral oils, such as would be used to adulterate linseed oil, will flash at from 380° to 420° F., so that the flash point is one of the best tests for detecting the adulteration of linseed oil with mineral or rosin oils.

Proportion of Mineral or Rosin Oils in Linseed Oil.—To determine the proportion of mineral or rosin oils in adulterated linseed oil, place 10 grammes in a beaker with a little water and alcohol, then add some caustic soda, and boil for some time, stirring at intervals; the linseed oil becomes saponified, while the adulterants are not acted on; after about an hour's boil the mass is allowed to cool a little, then it is poured into a separating funnel, and some petroleum ether is added, which will take up the mineral oil and form a layer on the top of the aqueous layer; after allowing the two layers to separate completely, the bottom layer is run off, and the top layer is washed quite free from all trace of the soap formed by the action of the alkali on the linseed oil by several treatments with warm water. The ethereal layer is then run into a weighed glass, the ether evaporated off, and the residue of mineral oil weighed. Whether the residue is mineral or rosin oil must be judged from the nature of the residual oil after evaporating off the ether; if this is heavy and viscid, and smells of rosin when heated, then rosin oil is present; if the residual oil is light, then mineral oil is present.

Cotton and other Fat Oils in Linseed Oil.—The detection of cotton-seed, niger-seed, or other fat oils in linseed oil is much more difficult, but much valuable information on this point will be gained by noticing the behaviour of the oil with strong sulphuric acid, the character of the mass formed, and the temperature which the mixture of acid and oil attains. The character of the soap formed on boiling the oil with caustic

soda, the appearance, melting point, and combining equivalent of the fatty acids which may be obtained from the soap so formed are also valuable indications of the character of the fatty oil adulterants.

Driers in Boiled Oil.—About 25 grammes are boiled with a little dilute hydrochloric acid, with constant stirring, for about half an hour; the mass is allowed to stand to separate; the bottom acid layer contains the driers added during the boiling of the oil; this is run off and tested in the usual way, then the oil is boiled with caustic soda until it is saponified, and then the mass is treated in the separating funnel, as described above, to separate the mineral or rosin oil used to adulterate the boiled oil. The aqueous layer which has been run off may be acidified, and the acids obtained tested for rosin by Gladding's test.

BOILED OIL SUBSTITUTES.—Many substitutes are offered for boiled oil, some of which have been patented. In composition they vary greatly, and it is not possible to do more than briefly indicate their general features. Some are mixtures of boiled oil, rosin, turpentine, and rosin oil; others more closely approach an oil varnish in composition, being made by melting rosin, then mixing it with hot oil and thinning down with rosin spirit. Some are made by preparing a compound of lime or alkali with rosin spirit or turpentine.

The quality of these products varies very much. None of them are equal to good boiled oil, although one or two very nearly approach it; others are but inferior substitutes, and cannot be recommended even for inferior work. It is not possible to deal more particularly with these boiled oil substitutes in this book.

POPPY OIL.—This oil is obtained from the seeds of the poppy (*Papaver somniferum*) by pressure, or it may be extracted by means of solvents. This oil, although a very good drying oil, is not largely used, chiefly because its price does not allow it to compete with linseed oil. Artists make use of it on account of its paleness in colour not interfering so much with pale tints as linseed oil does, its price not being so much an object with them as it is with house painters.

Poppy oil is usually of a pale straw colour, very limpid, has little or no colour when fresh, and a pleasant taste; the oil is free from the narcotic properties for which the plant itself is famous. In specific gravity it ranges from 0·924 to 0·927. It solidifies at $-18°$ C. It is soluble in about four times its volume of boiling alcohol, and twenty-five times its volume of

cold alcohol. Mixed with strong sulphuric acid (Maumené's test), the rise in temperature is about 88° to 90° C. It takes about 19 per cent. of caustic potash (K O H) to saponify it, and it absorbs about 134 to 137 per cent. of iodine.

HEMPSEED OIL. — The hemp plant (*Cannabis sativa*) yields a roundish greenish-grey seed, very familiar to lovers of canaries, from which, on expression, an oil is obtained that is used for painting. The yield of oil varies from 15 to 25 per cent.

Hempseed oil, when fresh, has a greenish-yellow tint, but on keeping it slowly turns to a brownish-yellow; its odour and taste are rather unpleasant. Its specific gravity ranges from 0·925 to 0·931. It becomes turbid at a temperature of – 15° C., but does not set completely solid until a temperature of – 25° C. is attained. Strong sulphuric acid has a vigorous action on it, the increase in temperature being about 100° C. It absorbs from 143 to 144 per cent. of its weight of iodine, which indicates that it contains a large proportion of linoleic acid (linolic and linolenic acids), and shows that its drying properties must be good.

In this country hempseed oil is rarely used as a paint oil, its price being against it; still it has been mixed with linseed oil, and it is difficult to obtain the latter free from it, owing to the Russian linseed growers mixing hempseed with the linseed. In Russia, and other places where hempseed is grown, the oil is used rather largely for painting.

WALNUT OIL.—The common walnut, the fruit of the walnut tree (*Juglans regia*), contains about 50 per cent. of its weight of an oil possessing drying properties. The process of extraction of this oil is as follows:—

The nuts are collected and placed in heaps for a period of about three months, when they begin to decompose; they are then crushed and pressed; this gives "virgin nut oil," often used as a food oil as well as a paint oil. The nuts still contain some oil, which is extracted by grinding the cake with hot water and again subjecting it to pressure; the oil so got is known as "fire-drawn nut oil."

Walnut oil is usually of a pale yellowish-green tint, but can be prepared almost colourless from fresh kernels. The specific gravity varies from 0·925 to 0·927; it begins to be turbid at a temperature of – 15° C., but becomes solid only when at a temperature of – 25·5° C. Strong sulphuric acid causes the evolution of some heat, the increase in temperature being 101° to 103° C. It will absorb about 144 per cent. of iodine, pointing

to its containing linoleic (linolic and linolenic acids) in large proportion.

It is a powerful drying oil; some authorities say that it is superior to linseed oil in this respect; at all events, it is quite equal to it in drying power. It is chiefly used by artists, as it is pale in colour, and can, by bleaching, be obtained almost colourless.

Its greater cost prevents its coming into extensive use as a substitute for linseed oil in house painting.

CHINESE WOOD OIL, or **TUNG OIL,** is obtained by cold pressure in a somewhat primitive manner by the use of wooden presses from the seeds of the Tung tree (*Elæococca vernica*), a member of the Euphorbiaceæ, a group of plants which grow very extensively on the banks of the Yangstze river, in China. The seeds yield 35 per cent. of their weight of the oil. The oil, when of good quality, is pale amber in colour, somewhat dull in appearance, but lacking that brightness which is seen in rape or cotton-seed oil. It has a peculiar and characteristic nutty odour and unpleasant taste. Its specific gravity at 60° F. is 0·940; at 212° F., 0·8871. It is rather viscous, being slightly more so than linseed oil, the viscosity at various temperatures being as follows:—At 70° F., 150; at 120° F., 98; at 150° F., 52; and at 212° F., 22. Mixed with strong sulphuric acid it forms brownish clots, and gives rise to a considerable increase of temperature, a mixture of 20 parts of oil with 8 parts of strong acid rising to 182° F. It takes 17·78 per cent. of caustic potash to saponify it; this points to the oil containing acids of high molecular weight. It contains a small quantity of free acid, about 1 to 3 per cent.

The chemical composition of this oil has not as yet been fully worked out. To one of its constituents the name of elæomargaric acid has been given.

It absorbs 93 per cent. of its weight of bromine, or 120 per cent. of iodine.

There are both soluble and insoluble fatty acids in this oil. When subjected to the Reichert distillation test, 10 grammes of the oil give a distillate which has an acidity equal to 16·2 c.c. decinormal caustic soda, while there are 88·7 to 90 per cent. of insoluble fatty acids.

Poured in a thin film over a glass plate it takes about two days to dry, being, therefore, quicker in its drying power than raw linseed oil, which takes about three days to dry. The dry film left by Chinese wood oil has a different appearance to that left by linseed oil; it is whiter, duller, and more opaque, which

is rather against its use in painting, and moreover the coat or film is rather crinkled and not smooth. Linseed oil leaves a smooth and bright film. By dissolving a little litharge in the oil, the opacity of the oil is removed, but the film still remains rather crinkled.

Heating Chinese wood oil appears to have no material influence in accelerating its drying power.

The behaviour of Chinese wood oil under heat is peculiar, and sharply distinguishes it from other oils. Maintained at a temperature of 212° F. for some days it slowly gelatinises, the jelly which is formed not being liquefied by heating. Heated up it, like all other oils, becomes thinner and more limpid; it does not darken so much in colour as does linseed oil under the same circumstances; when heated to about 550° to 560° F. it sets almost immediately into a clear transparent jelly, which is permanent on exposure to air, and has an appearance and consistency recalling that of india-rubber. This jelly is not melted by subsequent heating, and it is quite insoluble in hot oil, benzol, turpentine, petroleum spirit, alcohol, and similar solvents.

This peculiar behaviour of Chinese wood oil to heat throws it at once out of court for varnish making by the ordinary process, but the property might cause the oil to be of service to floorcloth, linoleum, and rubber manufacturers.

The oil does not appear to possess much solvent property for driers, especially for the linoleates and resinates of lead and manganese. There may be prepared from the oil preparations of lead and manganese, similar to linoleates, which act more efficiently as driers to linseed oil than any other preparation. The use of these preparations has been described in an English patent, where they are called "tungates."

Boiled up with caustic soda it yields a softish soap, which tends to become darker on exposure to air. Caustic potash yields a brownish soft soap.

When exposed to light for some time, the length of which depends upon the season of the year, the oil slowly becomes solid. The process begins with a deposition of solid stearin-like particles, and continues until the whole mass becomes solid; and the colour changes from amber to white. On heating, the solid melts, but the fluid on cooling resolidifies. In thus solidifying on exposure to light, Tung oil differs from other oils. To this feature is probably due the turning white of a film of Chinese wood oil on drying.

Tung oil is soluble in all solvents like benzene, petroleum spirit, ether, &c., and in hot alcohol and hot glacial acetic acid.

THINNERS OR SOLVENTS.

The "thinners," as they are commonly called by painters, or solvents, as turpentine, coal-tar naphtha, shale naphtha, petroleum spirit, benzoline, benzene, methylated spirit, are volatile bodies boiling at comparatively low temperatures, and consequently easily convertible into vapour by heat; and as easily reconvertible to fluid by abstraction of heat. As the boiling points and rate of distillation of these thinners vary with the different bodies, and those of turpentine, benzene, and methylated spirit are constant, they form a valuable means of determining the purity and quality of these bodies.

The boiling point and rates of distillation can be easily determined in one simple experiment carried out in the following manner:—

A complete apparatus for carrying on distillation consists of three parts:—First, a vessel which contains the liquid to be distilled; this is known as the *retort* or *still*. Second, the apparatus or condenser in which the vapour or gas given off from the liquid in the retort is condensed again into the liquid form; this is known as the *condenser*. Thirdly, the *receiver*, in which to collect the distillate.

Fig. 20.—Retort.

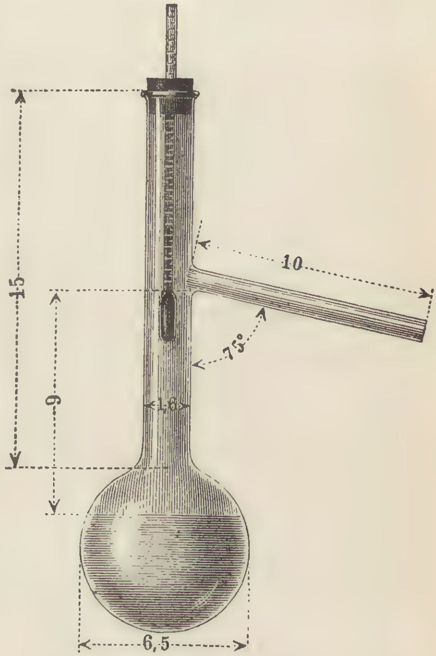


Fig. 21.—Distilling flask.

The **retort or still**.—Little need be said about this. The student will find the familiar appliance known as a retort (Fig. 20) of most service, though in some cases a flask fitted

with a delivery tube to carry the vapour off may be used. Flasks are made especially for distilling, which have a tube sealed in the side to carry off the vapour (Fig. 21). The sketches show the shape of these pieces of apparatus. A flask or retort to hold 4 ozs. is a convenient size to use. The figures given on Fig. 21 are centimetres.

Sometimes it is necessary to carry on the distilling at specified temperatures, or to make observations of the temperatures at which liquids boil and distil. For these purposes a thermometer is fitted in the retort or flask which is used, as shown in Fig. 21. The method of fitting in thermometers by chemists varies; some arrange it so that the bulb is near the exit of the vapours from the retort or flask, and thus one measures the temperature of the vapour as it comes off. Other chemists prefer to use retorts and to have the bulb of the thermometer immersed in the liquid which is being distilled, and thus one measures the boiling point of the liquid. A great deal depends upon what is wanted; if observations of boiling points only are needed, then the immersion of the thermometer bulb in the liquid is, in the writer's opinion, decidedly preferable.

When it is desired to fractionate the liquid into constituent parts, the use of a fractionating flask (Fig. 21), with the thermometer close to the side tube, often gives the best results.

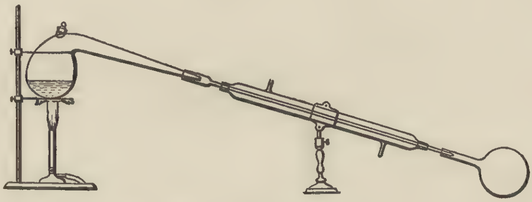


Fig. 22.—Liebig's condenser.

The second part of the distilling apparatus is the **condenser.** In a chemical laboratory the most convenient form is known as Liebig's, which is shown in Fig. 22. It consists of two long tubes, best made of glass, fitted one inside the other. The inner one is the longest; it is connected at one end with the retort, and at the other end with the receiver; hence it carries the vapours from the retort to the condenser. In the space between the two tubes cold water is made to circulate, to cool down the vapours as they pass along the inner tube. This condenser may be used in any position that may be most advantageous accord-

ing to the operations which are going on; generally it is placed in an inclined position, though at other times the vertical position is preferable. The water should flow in at the bottom and out at the top of the condenser.

Condensers are also made consisting of a worm immersed in a vessel of cold water, the vapours passing in at the top, while the condensed liquids flow out at the bottom. There is no material advantage in this form over the Liebig's condenser.

The remaining part of the apparatus needs but few words. It simply consists of any convenient vessel to receive the distillate. A flask is most convenient, especially when volatile liquids are being dealt with.

It is a good plan, especially in dealing with paints, varnishes, petroleum spirits, and similar inflammable liquids, to immerse the retort or still in a metal vessel which acts then as an air bath. This is done to guard against disaster in case the glass retort should crack during the operation, the liquid will simply flow into the metal bath and no serious damage will be done, whereas otherwise it might have flowed over the Bunsen burner and in doing so take fire, then flowing over the laboratory bend do some damage. The writer has seen accidents occur in this way.

The drawing (Fig. 22) shows a complete arrangement for distilling, but without a thermometer being inserted in the tubulure of the retort.

Having fitted up the apparatus, place in the retort 100 c.c. of turpentine and heat slowly, watching the thermometer; it will rise to about 310° F. (156° C.), and then the turpentine will boil; the temperature at which this happens is called the "boiling point." The turpentine passes into vapour; this flows through the condenser, is there cooled, and collects in the receiver as a liquid. Notice that after the turpentine begins to boil the thermometer scarcely rises at all, and that nearly all of the turpentine passes over before the temperature has reached 320° F. In first-class grades of turpentine all will pass over; in low grades a small yellowish residue, rosin, is left behind.

The same experiment may be tried with rosin spirit, but this difference will be observed that the thermometer continues to rise during the whole of the time. It may begin to boil at about 260° F., and before the end of the distillation the temperature may rise to 420° F. Samples of rosin spirit vary very considerably in regard to their boiling points and rates of distillation. It is a good plan to collect every 10 per cent. which comes over, and note the temperature in each case.

In the same way benzoline, petroleum burning oil, coal-tar naphtha, and methylated spirit should be tried, and any differences in the boiling point and temperatures of distilling noted. It is a good plan for the student to make various mixtures of thinners, and notice the boiling points and distilling temperatures of them. The proportion of thinners in paints and varnishes can be determined by distilling known quantities in a retort in this way.

TURPENTINE.

"Turpentine" is the term which was originally given to some resinous exudations from various species of pine and other coniferous trees, but of late years this term has been used to distinguish a volatile liquid obtained from the crude turpentines by distillation; formerly this liquid was known as "oil of turpentine," or "spirit of turpentine," and occasionally it is still so named; it is also known shortly as "turps." The crude turpentines are but of small value commercially, and some are only used in medicine. There are many varieties, such as Venice, Strassburg, Canadian, China, Aleppo, &c. Each of these has a soft resinous character and an aromatic odour; when distilled with steam they are decomposed into a volatile spirit and a solid residue, rosin, or colophony.

Under the term "turpentine" will be described the liquid spirit used by painters and varnishmakers.

There are three varieties of turpentine met with in the English market—viz., American, French, and Russian. All these are derived from various species of pine trees.

American turpentine is derived from two or three species of pine chiefly from the swamp of Georgia pine (*Pinus australis*), which grows in extensive forests in North and South Carolina, Georgia, and Alabama, the former State being the largest producer of turpentine. Turpentine is also obtained from the loblolly pine (*Pinus tæda*).

In winter, which extends from November to March, gangs of men proceed to the forests for the purpose of collecting the resin; for this purpose the trees are boxed—that is, a cavity is cut into the side of the tree, about 1 foot from the ground; the boxes have a capacity of about 2 or 3 pints. Sometimes three boxes will be made in a tree, but care is taken not to touch the heartwood, as such a proceeding would certainly kill the tree. The upper part of the box is always kept free from resin, and is frequently chipped so as to expose fresh surfaces of wood, which

causes the resin to flow more freely. About March, the sap begins to flow and to collect in the box on the sides of the cut surfaces; that which collects in the box is called "dip," while that which collects on the sides is known as "scrape." That which collects the first year in a box is known as "virgin dip," and is always collected separately. The crude resin is known commercially as "gum thus," and is exported for use in making varnishes. Most of the resin is, however, treated locally for turpentine and rosin, although it would be better to send it to some large works for treatment.

Turpentine is obtained from the crude resin by placing it in a still; into this still passes a steam pipe from a steam boiler, while out of it passes a pipe in connection with a worm condenser; a manhole on the top serves for the purpose of filling the still, while a large pipe at the bottom serves to run off the residual rosin; the still is heated by fire. When sufficient resin has been placed in the still the fire is lighted, and when the temperature has attained a little above the boiling point of water, a current of steam from the boiler is sent in; the turpentine passes over into the worm condenser and condenses along with water from the steam; when no more turpentine comes over, the rosin left in the still is run off into barrels, when the still is ready for another charge. The turpentine is often purified by a second distillation. The appliances in use are generally of a crude description.

French Turpentine.—This variety is obtained from the maritime pine (*Pinus maritima*), which grows very extensively in the south-west of France, especially in the Departments of Landes and Gironde. The industry in these districts is conducted on a rather more scientific principle than in America. The trees are cut in February or March, and the sap is caused to flow into an earthenware vessel placed at the foot of the tree. The trees are tapped for five years in succession; then they are not touched for a few years; after which tapping commences again; when the tree has got somewhat exhausted, the final tapping takes place, and a large yield of resin is obtained, but the tree is killed. It is felled, and another planted in its place.

The crude resin is placed in the still, 66 gallons being the usual charge; it is then heated by fire until a temperature of 135° C. (275° F.) is attained; when a current of steam is passed into the still, turpentine begins to come over and to condense along with the water from the steam in the worm condenser; the condensed products pass into a suitable receptacle, in which the water gradually settles to the bottom, while the turpentine

rises to the surface; the latter is skimmed off and run into other narrow-mouthed vessels, in which it is allowed to stand for several days, during which the remaining water and other impurities settle out. The yield of turpentine is rather more than one-fifth that of the crude resin employed.

French turpentine is almost entirely consumed in France; very little is now exported to England.

Russian turpentine is obtained chiefly from the Scotch pine (*Pinus sylvestris*). The method of obtaining it does not differ essentially from that adopted in extracting American or French turpentine, although there are some minor differences in the method of tapping the trees and collecting the crude resin, and in the manner of distilling the turpentine, which is usually done in a rather crude manner.

Russian turpentine differs slightly in properties from American and French turpentines.

Turpentine is a hydrocarbon having the formula $C_{10}H_{16}$; there are, however, a number of isomeric compounds known which have the composition represented by the above formula. These bodies have been named the terpenes; they are derived, as well as the three varieties of turpentine already described, from natural resins or from various natural oils.

Commercial French and American turpentine is a water-white limpid liquid, with a peculiar and characteristic odour that distinguishes it from all other bodies. The specific gravity ranges from 0·864 to 0·870, but usually is about 0·867. French turpentine is a little more uniform than American turpentine in this respect. It begins to boil at from 150° to 160° C., and is completely distilled at 170° C. If the sample be fresh, there is little or no residue left behind, but old samples generally leave a slight residue of resinous matter, which in any case does not amount to more than 1 per cent. of the turpentine.

Turpentine is readily combustible, burning with a smoky flame, a peculiar and characteristic odour being evolved. The flashing point of ordinary turpentine is 36° to 38° C. (97° to 100° F.).

Turpentine is readily miscible with ether, carbon bisulphide, alcohol, benzene, and petroleum spirit, but it is insoluble in water. It is a good solvent for oils, fats, resins, &c.

On exposure to the air in bulk, turpentine absorbs oxygen slowly from the atmosphere, becoming thick and viscid or fatty in appearance. A prolonged exposure causes the turpentine to become resinous, part of the turpentine volatilising during the exposure. In thin layers, such as would be formed when

turpentine is spread over a surface with a brush, a condition of affairs which occurs in painting, there is less oxidation, as a larger proportion of the turpentine volatilises away, and the oxidation of the residue is more complete, so that a hard resinous product is the result. This property distinguishes turpentine from all the other spirituous liquids used by the painter and varnishmaker; these evaporate completely away, and consequently leave no residue behind which can act as a binding agent for the pigment or colouring matter of the paint, whereas the resin left when turpentine is used acts as a binding agent, and fixes or fastens the pigment of the paint on the surface over which it is spread. American has greater absorbing powers for oxygen than French turpentine.

When repeatedly distilled with strong sulphuric acid, turpentine becomes polymerised. Generally two bodies are formed. One of these has been named terebene, which has the same formula ($C_{10}H_{16}$) as turpentine, and, when pure, boils at 160° C. The other body has been named colophene, has the formula $C_{20}H_{32}$, and boils at 300° C. It constitutes the main product of the reaction. This property of polymerisation, which is essentially a conversion from a spirit boiling at a low temperature into a spirit boiling at a high temperature, distinguishes turpentine from any of its substitutes.

Nitric acid acts very energetically on turpentine, the result varying with the strength of the acid used. If strong enough the turpentine may take fire; in any case, various oxidation products are obtained.

Chlorine, bromine, and iodine act with great energy on turpentine; *great care* must be taken in bringing these bodies into contact with one another, or explosions may occur.

Turpentine has a strong action on polarised light, a property which distinguishes it from benzene, petroleum spirit, and rosin spirit. French turpentine rotates the ray to the left, its specific value being 30°; it is fairly constant, showing that French turpentine has a very uniform composition; this fact is also shown by its regular specific gravity and by its steady distillation temperature. The specific rotation of the pure terpene, terebenthene, is 40°. American turpentine rotates the ray to the right, but the variation in the value in different samples is very great; ordinary commercial samples give specific values ranging from +8° to +16°; the pure terpene has a specific rotation of +21·5°. It is quite possible that American turpentine contains a small quantity of lævo-terpene, the quantity of which varies in amount, and, consequently, the specific rotation must vary also.

Burmese turpentine, from *Pinus khasyana*, which resembles French and American turpentine in its general properties, differs by having a strong and uniform rotation.

Russian turpentine resembles American turpentine in many of its properties, such as solvent and soluble features, action of nitric acid, sulphuric acid, chlorine, &c. It is rather more variable in composition and specific gravity, which latter varies from 0·862 to as high as 0·873. It begins to boil at about 156° C., but is not completely distilled below 180° C., the great bulk passing over between 172° and 174° C.; this greater range of distilling temperature points to a more complex composition than that of other turpentines. It has an odour resembling that of American turpentine, but differing slightly therefrom. It is rather more volatile. It rapidly absorbs oxygen from the atmosphere, becoming very viscid; partly on this account, and partly on account of its stronger odour, Russian turpentine has not come so much into use in making paints. It is said to induce headache when being used; this will depend a great deal on the physiological idiosyncracy.

Russian turpentine exerts a strong rotary action on polarised light, the specific value varying as much as from 15° to 23°, while the pure terpene, sylvestrene, has a specific rotation of 19°, which shows that the commercial turpentine must contain terpenes of higher rotary power, the amount of which varies in different samples. In all other properties Russian turpentine resembles American turpentine.

Of late years a great many substitutes for turpentine have been placed on the market under a variety of fancy names—"patent turpentine," "turpentyne," "turpenteen," &c.

Turpentine is frequently adulterated, the adulterants usually added being petroleum spirit, shale naphtha, rosin spirit, and coal-tar naphtha. The fact of the adulteration and the nature of the adulterant added is easily ascertainable, but the question of proportion of adulteration is more difficult to ascertain, and demands the exercise of some considerable care and skill on the part of the analyst.

The property of acting on polarised light distinguishes turpentine from all bodies used to adulterate it, the specific value for each variety of turpentine has already been given, the presence of other bodies tends to reduce these values in proportion to the extent of the adulteration.

The specific gravity is a good indicator of adulterations, as, with the exception of coal-tar naphtha, the addition of other spirits tends to cause it to vary from the normal average of 0·867.

The addition of any of the adulterants named has a material influence on the temperature at which the turpentine begins to boil and those at which it distils. Genuine turpentine does not begin to distil below 150° to 156° C., the thermometer rising slowly from this point. In the case of French or American turpentines all is distilled over before the temperature attains 170° C., while with Russian turpentine the temperature may reach 180° C. before all is distilled. The greater portion of the turpentine passes over between 158° and 161° C. with American or French turpentines, while at least 93 to 95 per cent. passes in the case of Russian turpentine the great bulk passes over between 170° and 175° C. Adulterated turpentine begins to distil much below 150° C., in some cases below 80° C., according to the nature of the adulterant added; from the point at which the sample begins to distil there is a gradual increase of temperature, the thermometer rises slowly, and in some cases the distillation is not complete at 200° C. By comparing the temperature at which the sample distils with the distillation temperatures of the possible adulterants as given in the descriptions of these bodies, some idea of the nature and the approximate amount added of the adulterant may be obtained.

The adulteration of turpentine by the addition of petroleum or shale naphtha may be detected by a considerable reduction in the specific gravity of the sample, by its low boiling point, and its taking fire at between 60° and 70° F., turpentine not taking fire below 100° to 110° F. Sometimes petroleum burning oil or paraffin burning oil is added; in this case the gravity will be reduced, the boiling point and rate of distillation will be altered, and all will not be distilled over at from 160° to 170° C. The flash point may range from 73° to 90° F., according to the character of the oil added.

The proportion of adulteration is difficult to ascertain; approximately it may be determined by the following method which is based on the fact that while turpentine can be distilled in a current of steam, the shale and petroleum naphthas and oils cannot. Into a retort is placed 100 c.c. of the turpentine, which is gently heated by means of a Bunsen burner; through the retort is passed a current of steam generated by boiling water in a flask, the steam from which is passed through the turpentine in the retort. The distillation is carried on until no more spirit passes over, a Liebig's condenser being used to condense the vapours which pass over. Under these conditions genuine turpentine does not leave more than 0·2 per cent. of unvolatile residue, if fresh; old samples may leave as much as 0·5 per cent.

Any residue above 0·5 per cent. which may be left in the retort may be considered to be evidence of adulteration, and its nature can be ascertained by a few experiments. Those portions of the naphthas from either shale or petroleum which are volatile below 100° C. will pass over with the turpentine; in this event the distillate will have a specific gravity below 0·800, as a rule.

Rosin spirit is rather more difficult to detect when it is used for adulterating turpentine. It increases the specific gravity. Its wide range of distilling temperatures and its odour are sufficient to detect it, but there is no satisfactory method of determining the proportion which may have been added; the steam distillation process gives the best results.

Coal-tar naphtha is not much used for adulterating turpentine; it has much about the same specific gravity, but takes fire at the ordinary temperature, has a wider distilling range of temperature, is more volatile, and has a peculiar odour.

ROSIN SPIRIT.

When rosin is subjected to distillation, either by fire heat alone or with the aid of superheated steam, there is obtained, as one of the products, a light volatile spirit, which, when crude, has a dark brown colour. As a rule, the proportion of rosin spirit obtained is small. When fire heat alone is used, only about 3 per cent. is obtained; if superheated steam is employed, from 10 to 15 per cent. is obtained. This rosin spirit is refined by treating first with sulphuric acid, next with caustic soda, and then redistilling the washed spirit.

Rosin spirit is a limpid, water-white to straw-coloured liquid; the colour varies with the degree with which the refining has been done. It has a peculiar and characteristic terpene odour. Its specific gravity varies considerably, from 0·876 to 0·883, but it is invariably heavier than turpentine. Exposed to the air, it volatilises in part and partly oxidises, the result of the oxidation being the formation of a resinous residue, as is the case with turpentine, but not to the same extent. It flashes at from 36° to 38° C. (97° to 102° F.).

On heating in a retort or flask, rosin spirit enters into ebullition and distils over; the temperature rises during the whole of the time of boiling. The temperature when boiling begins, the rapidity of distillation, and the temperature below which it is all distilled over vary much.

It may be laid down as a rule that a spirit completely dis-

tilling below 240° C. is better for use in paint-making than one distilling above that temperature. The continual increase of temperature during the process of distillation is a point of distinction from turpentine, and points to complexity in the composition of rosin spirit.

Rosin spirit is insoluble in water and alcohol, but is soluble in ether, or a mixture of alcohol and ether, as also in turpentine, chloroform, and petroleum spirit. Nitric acid acts on it rather less energetically than on turpentine, forming with it a dark scarlet mixture; hydrochloric acid has but little action. Sulphuric acid forms a dark red mixture; probably there is some polymerisation.

In composition rosin spirit is a mixture of several hydrocarbons, the exact nature of which has not yet been thoroughly worked out. From rosin spirit has been isolated heptine, C_7H_{12}, a colourless, limpid liquid, having a specific gravity of 0·8031, and boiling at 103° to 104° C.; on exposure to the air it absorbs oxygen. Sulphuric acid polymerises it with the formation of diheptine, $C_{14}H_{24}$, which boils at from 235° to 250° C., and which, on exposure to air, rapidly absorbs oxygen and resinifies. Heptine, exposed to air in the presence of water, forms crystals, having the formula $C_7H_{12}(OH)_2H_2O$. It combines with bromine to form the compound $C_7H_{12}Br_2$, which is a heavy yellow oil. In light rosin spirit, containing constituents boiling below 100° C., there have been found hexylene, C_6H_{12}, and amylene, C_5H_{10}.

Rosin spirit is the best substitute for turpentine known, and is capable, when of good quality, of replacing it for all purposes. The chief objection to it lies almost entirely in its odour, which is not so pleasant as that of turpentine.

Then again, if sufficient care has not been taken in refining it, it is apt to contain traces of rosin oil, which would prevent it from drying properly. The specific gravity of a good sample of rosin spirit should not exceed 0·880, and all should distil below 250° C.; it may be taken for granted that any residue left at temperatures above 250° C. will consist chiefly of rosin oil, which reduces the value of the rosin spirit, owing to its want of drying properties. Rosin spirit is used in making some of the turpentine substitutes which are now so common.

The only possible adulterants for rosin spirit are shale naphtha and petroleum benzoline, the presence of which can be ascertained by the application of the tests for specific gravity, flash point, and distillation temperatures, as in the case of turpentine.

Rosin spirit is largely used in making cheap varnishes, using rosin as the body gum, and, occasionally, colouring the varnish with pigments.

SHALE SPIRIT, OR SHALE NAPHTHA.

When the shale found in the south of Scotland, in the district lying between Glasgow and Edinburgh, is distilled at a comparatively low temperature, there is given off a quantity of tarry matter known as "crude oil;" this is a product of very complex composition, which on redistillation gives a purer product known as "once-run oil." This is further refined by treatment, first with sulphuric acid (to remove basic impurities), and then with caustic soda (to remove acid impurities); finally it is distilled, when it yields three chief products—"green naphtha," "twice-run light oil," and "green oil." The two latter do not interest painters.

The "green naphtha" is refined by treatment with sulphuric acid, caustic soda, and redistilling, when there is obtained a very limpid water-white liquid, known commercially as "paraffin naphtha" or "shale spirit;" the yield is about 5 per cent. of the crude oil.

Shale naphtha is a water-white very limpid liquid, having a specific gravity of 0·730 to 0·760, and a slight odour. It is insoluble in water and alcohol, but mixes freely with ether, turpentine, benzol, &c., while it readily dissolves all oils (except castor oil), many of the resins (such as gum dammar) in the natural state, and nearly all when they have been partially decomposed by fusion. It is very volatile, and, unlike ether, turpentine, or rosin spirit, evaporates without leaving any residue behind.

It is inflammable, readily taking fire at ordinary temperatures, which is one objection to its use. It begins to boil below 100° C., and is generally completely distilled over below 190° C., the range of temperature and the proportion which distils over varying with different makers.

Acids and caustic alkalies have no action on shale spirit. It absorbs a small quantity of bromine or iodine.

Shale naphtha is a complete mixture of hydrocarbons belonging to the two series, paraffins and olefines, the latter forming about 60 per cent. of the naphtha. There have been found hexene (C_6H_{12}), heptene (C_7H_{14}), octene (C_8H_{16}), and nonene (C_9H_{18}) among the olefines; hexane (C_6H_{14}), heptane

(C_7H_{16}), octane (C_8H_{18}), and nonane (C_9H_{20}) among the paraffins; but other members of these two series are present.

Shale naphtha is largely used as a substitute for turpentine, and, on the whole, is a good material for the purpose. It is distinguished from both turpentine and rosin spirit by its much lower gravity, its great inflammability, its indefinite boiling point, and by not being completely distilled in a current of steam as is turpentine.

Benzoline, Benzine, or Petroleum Spirit. — When the petroleum obtained from the oil wells of North America is subjected to distillation three products are obtained — viz., "naphtha," "kerosine," and "residuum."

The "naphtha" is refined by treating with sulphuric acid, then with caustic soda, and distilling, when three products are obtained—viz., "gasoline," "benzoline," and "naphtha." The first, gasoline, is a very light product, having a specific gravity varying from 0·650 to 0·680, and is used only for special purposes. The other two products are sold indiscriminately under the names of "benzoline," "benzine," and "petroleum spirit." These products vary much in quality. They are water-white very limpid liquids, having a specific gravity ranging from 0·710 to 0·740, but heavier samples are met with.

In its general properties benzoline resembles the shale naphthas; what is generally sold under that name has a specific gravity of about 0·730; it flashes and takes fire at the ordinary temperature; it begins to distil at about 65° C., and is usually completely volatilised at 150° C.

In its general features, chemical composition, and uses petroleum spirit resembles shale spirit; it contains, however, a larger proportion of the paraffin hydrocarbons.

COAL-TAR NAPHTHA.

Coal-tar naphtha is not much used in paint-making, but in the preparation of varnishes it finds some use. In the operation of tar distilling several products are obtained, the proportion and nature of which depend partly upon the composition of the tar and partly upon the manner in which it is distilled. Among the products is a light oil or spirit of a dark brown colour, known as "naphtha" or "light" oil; in specific gravity it ranges from 0·840 to 0·940. Its odour is characteristic, but somewhat disagreeable. Its composition is complex, containing hydrocarbons of the paraffin and olefine series in small quantities, but its characteristic constituents are hydrocarbons of the

benzene series, such as benzene, C_6H_6; toluene, C_7H_8; xylene, C_8H_{10}; cumene, C_9H_{12}; durene, $C_{10}H_{14}$; besides these it contains ammonia, aniline, toluidine, and other nitrogenous bodies, alcohol, phenol, acetic acid, and sulphur compounds.

It is purified by re-distillation, when what is called "once-run naphtha" is obtained; this is further purified by treatment with sulphuric acid, which removes all the basic bodies, the hydrocarbons of the olefine and crotonylene series, and the higher members of the benzene series. After separating the acid from the semi-purified naphtha, the latter is treated with caustic lime or caustic soda, which removes all the oxygen and sulphur compounds; finally, the naphtha is well washed with water, and is then ready to be finally purified by a re-distillation.

Once-run naphtha has a specific gravity of 0·886 to 0·893, and is then raw material for the preparation of the benzols, solvent naphtha, and burning naphtha, as the commercial products are named.

The benzols are light products used in the manufacture of aniline dyes. Burning naphtha, which has a specific gravity of about 0·880 to 0·887, is sold for burning in out-door lamps, especially costermongers' lamps, although it has of late been largely displaced by the petroleum oils for this purpose.

Solvent or coal-tar naphtha is largely used in the india-rubber industry, and for making varnish. It is a water-white liquid, having a peculiar and characteristic odour of coal-tar hydrocarbons; in specific gravity it varies somewhat, the usual range being between 0·865 to 0·877. On being subjected to distillation it gives from 8 to 30 per cent. of distillate below 130° C.; as a rule, 90 per cent. distils over below 160° C. It burns with a very smoky flame, and is very inflammable, the flash point being about 120° F. It is miscible with alcohol, ether, turpentine, petroleum spirit, shale naphtha, and other similar solvents, while it is a good solvent for oils, fats, resins, and is almost the only solvent for coal-tar pitch and other pitches.

In composition it is very complex, but it consists chiefly of the three isomeric, para-, meta-, and ortho-xylenes, C_8H_{10}, cumenes, small quantities of paraffins and olefines, and, occasionally, traces of naphthalene. It is very inflammable, taking fire readily at the ordinary temperature, and burning with a very smoky flame. Its flash point is below 32° F.

Nitric acid has a strong action, and transforms the coal-tar hydrocarbon into the nitro-derivatives, nitroxylenes, $C_8H_9NO_2$, nitro-cumenes, &c. Hydrochloric acid, caustic soda, and caustic potash have no action on it. It is used in making cheap quick-

drying varnishes, rosin being the usual substance added to give the requisite coat; it is more volatile than turpentine, although it does not leave any residue behind it.

Commercial coal-tar naphtha is occasionally adulterated with petroleum or shale spirit, or with petroleum or paraffin burning oils; in every case the specific gravity is reduced. The addition of the petroleum and shale spirits causes it to distil at lower temperatures and a little more regularly, while the burning oils raise the distillation temperatures rather considerably.

Such additions may also be detected by treating the suspected sample with a well cooled mixture of sulphuric and nitric acids, which converts all the coal-tar hydrocarbons into nitro compounds, while the paraffin or petroleum oils are unaffected; if now water is added, the nitro bodies, being heavy, sink to the bottom, while the petroleum hydrocarbons, being light, rise to the top, and may be collected and measured. It should be pointed out that finding a small amount of such unchanged hydrocarbons does not necessarily indicate adulteration, as coal-tar naphtha naturally contains small quantities of paraffin hydrocarbons.

METHYLATED SPIRIT.

This important varnish solvent consists essentially of a mixture of two bodies, ethyl and methyl alcohols; the commercial product contains small traces of impurities inseparable from the process of manufacture.

Ethyl alcohol forms 90 per cent. of the methylated spirit. It is essentially a product of fermentation of starch and sugar, so that whenever grain, starchy matters, sugar, or fruits containing sugar are allowed to ferment, alcohol is always produced, and so we find it a constituent of beers, wines, and spirits, and to it is due the intoxicating effect of those liquors, from which it can be obtained by a process of distillation, and so it is often called "spirit of wine." Commercially it is obtained by distillation from the fermented liquor from corn, barley, and other cereals, hence it is sometimes called "grain spirit."

Pure ethyl alcohol is a colourless, very limpid liquid, having a pleasant odour and a hot burning taste. It is very volatile when exposed to the air, passing off completely and leaving no residue behind. It boils at 78·5° C. (173° F.), and distils over completely and unchanged at that temperature. It is only solidified when subjected to the very low temperature of −130° C. The specific gravity of pure alcohol at 15·5° C.

(60° F.) is 0·7935, but it has such an affinity for water that the preparation of a sample absolutely free from water is exceedingly difficult, so that the specific gravity given above may not be quite correct, but the error, if there be any, is small. Alcohol mixes with water in all proportions; if the two bodies are fairly pure the proportion of alcohol in such a mixture may be ascertained by simply determining the specific gravity. It mixes with ether, chloroform, turpentine, carbon bisulphide, and benzol, but not with petroleum products. It dissolves fatty acids and castor oil readily, but it has only a slight solvent action on the other fatty oils. It dissolves rosin and a few other resins, such as shellac, sandarac, mastic, more or less completely, but it will not dissolve the hard copals—*e.g.*, animi and kauri. It is a powerful solvent for coal-tar dyes and other bodies.

Its chemical composition is shown in the formula C_2H_5OH; when treated with oxidising agents, such as bichromate of potash and sulphuric acid, or manganese oxide and sulphuric acid, it is first transformed into aldehyde, which has the formula CH_3COH, and finally into acetic acid, which has the formula CH_3COOH.

The alcohol ordinarily met with in commerce is known as "rectified spirit of wine," this has a specific gravity of 0·838, and contains 86 per cent. of real alcohol; what is known as "proof spirit," has a specific gravity of 0·926, and contains 49 per cent. of real alcohol.

Alcohol alone is not used in the preparation of varnishes, as the high rate of duty levied by the Excise authorities prohibits its use for this purpose.

Methyl alcohol is a homologue of ethyl alcohol, and has the composition indicated by the formula CH_3OH. When pure it is a colourless liquid, very mobile and volatile, which has a fragrant spirituous odour, and boils at 55° C. Its specific gravity at 15·5° C. (60° F.) is 0·8021, but authorities vary a little on this point. It is miscible in all proportions with water, from which it is not easily separated; it also mixes freely with alcohol, ether, turpentine, &c., and possesses great solvent properties for resins, &c.

When subjected to the action of oxidising agents it is first changed into formaldehyde, $HCOH$, then into formic acid, $HCOOH$.

Methyl alcohol is obtained in large quantity in the dry distillation of wood. The wood is placed in iron stills or retorts in suitable furnaces, when there come over gaseous vapours, which condense, partly into an aqueous layer, and partly into a tarry mass. The aqueous layer, which has an exceedingly

complex composition, contains acid, alcoholic, phenolic, ethereal, and other compounds. When separated from the tar, treated with slaked lime, and subjected to heat, crude wood spirit distils over, while impure acetate of lime is left behind on the still.

The spirit is very impure, and is further treated by redistilling over quicklime, then treating with sulphuric acid (which removes ammonia and methylamine), and, finally, redistilling with lime.

Crude wood spirit, as obtained by the above process, is a liquid of complex composition, containing about 95 per cent. of methyl alcohol in the best qualities, although some samples do not contain more than 40 or 50 per cent. The following bodies are found in wood spirit, or wood naphtha, as it is sometimes called:—Methyl alcohol, $C\,H_3\,O\,H$; acetone, $(C\,H_3)_2\,C\,O$, specific gravity 0·772, boiling point 56·5° C.; allyl alcohol, specific gravity 0·8604, boiling point 96·5° C.; furfurol, ketones, &c.

The odour of wood naphtha is characteristic and somewhat unpleasant. It is due entirely to the impurities which are present in the spirit. Its taste, for the same reason, is extremely nauseous; hence the use of wood naphtha in making methylated spirit.

Wood naphtha is used for dissolving gums and resins in varnish-making, and it is worth noting that many of the gums are more freely soluble in the crude wood naphtha than they are in the pure methyl alcohol. The cause of this increased solvent power of the crude spirit must reside in the ethereal impurities it contains, many of which dissolve resins more freely than does methyl alcohol.

The following reactions serve to distinguish wood spirit from pure methyl alcohol:—Caustic soda gives a brown colour, sulphuric acid a red colour, which increases in depth on heating; mercurous nitrate gives a grey precipitate of mercury.

Methylated spirit is a mixture of 90 parts of rectified spirit of wine with 10 parts of wood spirit, and this mixture is permitted by the Excise authorities to be sold, under special regulations, for manufacturing purposes free of duty, the addition of the wood spirit rendering the spirit undrinkable. Of late years, however, owing to improvements in the manufacture of the wood naphtha, much of the nauseous taste is removed, and the methylated spirit now made is not so undrinkable. On this account the Excise authorities have recently compelled the addition of $\frac{1}{8}$ per cent. of petroleum oil to the methylated spirit, with the object of rendering it still more undrinkable,

but the use of the original spirit is still by special permit allowed.

The methylated spirit is usually sold at a strength of "64 over proof," and has a specific gravity of 0·821. It contains 90 per cent. of real alcohol. The meaning of the term "64 over proof" is that when 100 volumes of this spirit is mixed with 64 volumes of water, there is obtained "proof spirit," which is a spirit of such a strength that when mixed with gunpowder it will not set fire to the powder when a light is put to it. The term "proof spirit" is very vague, and should be done away with. It would be better to sell the spirit according to the actual quantity of alcohol it contains.

The strength of methylated spirit may be fairly accurately estimated from its specific gravity. Tables have been constructed showing the quantity of alcohol contained in spirit of different gravities. Space cannot be spared in this book for the reproduction of those tables, but the following table contains some information on this point which may be of use :—

Specific gravity at 60° F.	Per cent. of Alcohol.	Per cent. of Proof Spirit.	Specific gravity at 60° F.	Per cent. of Alcohol.	Per cent. of Proof Spirit.
0·79384	100	175·25	0·880	66·7	129·5
0·800	98	173	0·890	62·3	122·5
0·810	94·6	169·2	0·900	58·0	115·3
0·820	91	164·75	0·910	53·57	107·6
0·830	87·2	159·75	† 0·91984	49·16	100
* 0·8382	84	155·45	0·920	46·64	99·8
0·840	83·3	154·5	0·930	39·8	91·64
0·850	79·3	148·8	0·945	34·5	85·59
0·860	75·1	142·6	0·950	...	82
0·870	70·84	136			

Methylated spirit generally has an acid reaction, due to the presence of small quantities of acetic acid and aldehyde; besides these it contains traces of higher alcohols (amyl alcohol, propyl alcohol), oily and resinous bodies, ethereal compounds, and water.

Methylated spirit is used in making varnishes from shellac, sandarac, rosin, mastic, dammar, and other resins; such varnishes are very quick in drying owing to the volatility of the methyl ated spirit. It is also used in the preparation of enamel paints

* Rectified spirit of wine. † Proof spirit.

The quality of methylated spirit may be ascertained by distilling 100 c.c., when nearly all should be distilled below 100° C., the great bulk passing over between 80° and 90° C. The specific gravity is also a good indication of the quality, as shown in the table given above. In making any determination of the specific gravity, particular attention must be paid to the temperature at which it is determined, as small variations of temperature cause considerable alteration in the specific gravity; the standard temperature is 15·5° C. (60° F.). The actual determination may be made by means of an hydrometer, either the glass one, or the metal one, known as Sikes hydrometer, which is used by the Excise authorities, or the specific gravity bottle may be used.

Finish or methylated finish is methylated spirit containing about 3 ozs. of rosin to the gallon. For some purposes this may be used in the place of methylated spirit, as the Excise do not place so many restrictions on its sale. It may be distinguished from the pure spirit by its giving a very copious white precipitate when water is added to it.

On the Continent distilled animal or "Dippel's" oil is used for the denaturing (or rendering undrinkable) of alcohol, the use of this material has not been adopted in this country.

The flash point of methylated spirit varies from 57° to 60° F.

CHAPTER IX.

DRIERS.

It has long been a matter of observation among painters that paints made with white lead, orange lead, red lead, chrome yellows and oranges, and some other pigments, dry much quicker than paints made with other pigments, such as barytes, lamp black, ultramarine, &c. Further, it is known that when some substances, such as acetate of lead, acetate of manganese, red lead, manganese borate, &c., are added to paints and varnishes these become dry or hard much quicker than do paints, &c., that do not contain them; and, further, that linseed oil mixed or heated with such bodies dries much quicker. From this fact has arisen the plan of adding, in the manufacture of paints, varnish drying oils, siccative oils, and various substances, "driers" as they are called, for the purpose of facilitating the drying or hardening.

While the manner in which driers act upon the oil of the paint or varnish is not thoroughly known, it is thought they act by being carriers of oxygen from the air to the oil. The oil first acts upon the drier taking up oxygen from it, and in so doing becomes dry and hard; the drier having lost some oxygen is now ready to take up more from the air to replace that which it has lost, and having done so is ready to react with another portion of the oil, and this action goes on until the oil has absorbed as much oxygen as it can do. A very small quantity of "driers" will cause the drying of a large quantity of oil; from 0·5 to 1 per cent. of the weight of the oil is usually sufficient.

The rapidity of drying of oils, paints, and varnishes is proportioned to the quantity of drier used or dissolved in it; thus an oil which contains 2 per cent. of lead oxide will dry much more quickly than an oil which contains 1 per cent. Manganese compounds are more energetic drying agents than lead compounds. Driers which dissolve easily in the oil, such as the linoleates and resinates, are more active than those which, like red lead or manganese, do not dissolve in the oil.

When raw linseed oil is mixed with lead oxide, or manganese borate, very little of these is taken up and the rapidity of drying is not much increased. But if the oil be heated with them, they are more freely dissolved, and the treated oil dries much more rapidly. Hence probably arose the plan of "boiling" the linseed oil.

The substances described below in a brief form are used or added to paints as "driers."

Lead Compounds—Acetate of Lead.—*Sugar of Lead.*—This substance, which has the formula $Pb\ 2\ C_2\ H_3\ O_2\ 3\ H_2\ O$, is sold in the form of white lustrous crystals having a sweet taste. It is soluble in water. It dissolves in oil, especially under the application of heat, and is a fairly energetic drier. Ground up into a paste form, it is much used by painters to increase the drying of paint. Too much must not be used or the paint will dry too hard and be brittle.

Red Lead and **Orange Lead,** which have already been described, can act as driers, and are much used in the preparation of boiled oil and varnish. Their use tends to darken the oil very considerably. They are not very soluble in oil, and require it to be made hot before they will dissolve in it. Paint made with these two pigments dries very rapidly, and little or no boiled oil should be used in making it.

White Lead, Chrome Yellow, and indeed all pigments containing lead act as "driers" to the paint containing them.

Lead Borate.—This body, obtained by precipitating a solution of lead acetate with a solution of borax, has been largely used as a drier. It dissolves more freely in oil than red lead or litharge; hence oil made with it does not darken so much in colour and dries rather more quickly.

Litharge.—The lead monoxide, litharge, has long been used as a drier; it dissolves rather more freely in oil than red lead, and, therefore, does not lead to the production of such dark oils, while there is less "foots" produced.

Lead Linoleate.—Of late years the use of the linoleates and resinates of lead and manganese has much increased; they are called "soluble driers" on account of the fact that they dissolve completely in oil, so that no "foots" are produced; and, being soluble, no long heating of the oil is needed, so that paler oils can be produced. In fact, manganese linoleate under certain conditions can act as a bleaching agent, and so very pale drying or siccative oils can be produced. Lead linoleate is made by preparing a neutral soda soap from linseed oil and caustic soda, and pouring this into a solution of lead acetate. In some cases

the lead linoleate is sent out in the form of powder; in others it is melted into a resin-like form. When well made it should be entirely soluble in turpentine or chloroform, and dissolve fairly easily in hot linseed oil.

Lead Resinate.—This substance is made by making a soap from rosin and caustic soda, and adding it to a solution of lead acetate, or it may be made by melting rosin and sugar of lead together. It is sold either as a powder or in lump form, and, like the linoleate, is easily soluble in turpentine, chloroform, and hot linseed oil. It is a fairly effective drier.

Manganese.—The oxide of manganese, $Mn\,O_2$, has been much used as a drier, but it suffers from several faults; it is not freely soluble in the oil, and requires a high temperature to enable it to combine with the oil; it darkens the oil very much; and it produces much foots. It is a more energetic drier than lead oxide, a character which also belongs to all compounds derived from manganese oxide.

Manganese Borate is prepared by mixing solutions of manganese sulphate and borax, and collecting and drying the manganese borate which is precipitated; it is largely used as a drier. It dissolves fairly well in oil, does not produce much foots or darken the oil, and is very efficient as a drier.

Manganese Sulphate, Manganese Acetate, and **Manganese Chloride** have all been used more or less as driers, and work very well.

Manganese Linoleate is made by adding a solution of soap made from linseed oil to a solution of manganese sulphate. It is sold both in the form of powder and in lumps like rosin. It dissolves freely in turpentine and chloroform, and in hot linseed oil; it is a most effective drier

Manganese Resinate, made by pouring a solution of rosin soap into a solution of manganese sulphate, is sold both in the form of powder and in lumps. It resembles manganese linoleate in its properties.

Manganese Linoleate and **Resinate** may be classed amongst the most powerful of paint driers.

Ferrous Sulphate, or copperas dried by heating, is often added to varnishes as a drier, although its properties as such are not strong.

Linseed Oil that has been strongly boiled with a large proportion of driers, and then mixed with turpentine, forms a liquid drier which mixes freely with paint, and hence is very serviceable for the use of painters; it acts as an efficient drier.

Various combinations of the above driers with other bodies, such as zinc oxide, barytes, oil, &c., are often made and sold under the names of "patent driers," "siccatives," and other fancy names.

A fuller account of the various driers and their properties will be found in the author's *Manual of Painters' Colours.*

CHAPTER X.

VARNISHES.

A VARNISH is a liquid body which, when applied to a surface by means of a brush, dries up more or less quickly, leaving behind a highly lustrous coat of a very durable character. Varnishes are used to give additional protection to any decorative work from the action of the weather, or, in the case of much ornamental woodwork, to develop the beauty of the wood and to protect the surface from damage.

There are two kinds of varnishes—*oil varnishes* and *spirit varnishes.* The former are of an exceedingly durable character, and much used for woodwork of all kinds; generally they are slow in drying. Spirit varnishes are also good, but their merit is that they dry quicker, because in making them volatile bodies (such as methylated spirit, naphtha, and turpentine) are used.

Varnishes owe their quality to the use of certain natural bodies, resins, in making them, and to these both their lustre and protective properties are due.

The materials used in making varnishes comprise such bodies as drying oils, solvents or thinners, gums, driers, and colouring matters. The first two of these have already been described, as also the driers.

GUMS.—Out of many trees, particularly those grown in the tropical and subtropical regions, come exudations, at first liquid, but which soon set into a more or less hard mass, all of which are known by the generic name of "gums," notwithstanding that there is a marked difference in the composition and properties of these substances, as, for instance, gum arabic, gum thus, gum copal, gum kauri, gum sandarac, gum tragacanth, &c.

The gums may be divided into at least three groups—

1st, Gums proper,
2nd, Resins,
3rd, Rubbers,

each of which may be further subdivided.

The true gums, such as gum arabic (the type of a true gum), gum tragacanth, and a few others, are, like the resins, exudations from trees, and are collected much in the same manner.

They differ from resins in one or two important particulars. In the first place, they are more or less soluble in water; some, like arabic or acacia gums, are completely soluble; others, like gum ghatti, are partially soluble; while others again, like tragacanth, are not properly dissolved by water, although acted upon by that vehicle. The true resins are quite insoluble in water. On the other hand, the gums are quite insoluble in alcohol and similar solvents.

These gums are almost exclusively used for making water varnishes, or (as in water-colour painting and in some kinds of distemper work) as fixing agents to fasten the pigment on to the work.

Besides the gums proper there are used, in making water varnishes, gelatine or glue, dextrine or British gum, and albumen.

Gum Arabic.—The name of this gum is a misnomer, because it would indicate that it comes from Arabia, whereas but little, if any, now comes from that country; probably in early times it may have been obtained from that country, or, at least, imported through it, and hence the term "arabic" arose.

It is also known as gum acacia, from the trees which yield it, but gum arabic, despite its inappropriateness, is the name by which it is best known in the trade, and, therefore, it will be retained here.

The species of *Acacia* are profusely distributed throughout the tropical parts of Africa, Asia, and Australia, and are all gum producers. The gums vary a little in appearance and properties, but all are more or less soluble in water, and give with that solvent a strongly adhesive mucilage useful for a great variety of purposes. These gums are distinguished in the trade by terms descriptive either of their place of origin or of their quality, such as picked Turkey, white Sennaar, Senegal, Cape, Mogador, Indian Ghatti, Wattle, brown Barbary, &c.

Picked Turkey or *white Sennaar arabic* is the produce of *Acacia Senegal*, a tree growing in the Upper Nile regions and in Kordofan, where it is collected by the natives and shipped to Egyptian ports for exportation.

Gum Senegal is the produce of the same species of *Acacia*, and is collected in the French province of Senegal. This variety of gum is very varied in quality, ranging from a fine white gum to a dark somewhat reddish gum.

The best qualities of gum arabic are used for pharmaceutical preparations, confectionery, and other purposes, while the common qualities find a use in textile industries, varnish-making, and for making mucilages.

Besides the Acacias other trees yield gums which sometimes find their way into the English market, such, for example, as gum ghatti; these gums are not so good as true gum arabic. The gums from the Australian wattles, which are various species of *Acacia*, the principal trees being *A. decurrens* and *A. pycnantha; A. homalophylla*, *A. harpophylla*, and *A. Bidwilli* are of smaller importance. The quantity of gum obtained is rather larger than from African trees, and is of good quality.

The following description is nearly applicable to all the above varieties of gums. Gum arabic occurs in roundish or ovoid, or even vermicular masses of various sizes; the surface always has a glistening appearance; the colour varies from an almost colourless gum to a faint reddish or brownish tinted gum. While some pieces are transparent, many are simply translucent, and some are opaque; they are brittle and easily friable. Although this property is a variable one, the Australian gums being less friable than the others, and gum Senegal generally the most friable. These gums are quite free from odour, and their taste is slight. They are quite soluble in water; the best qualities take about one and a-half times their weight of water to form a thick viscid, highly adhesive mucilage, which is insoluble in alcohol; hence the addition of alcohol to the aqueous solution causes the precipitation of the gum. A solution of subacetate of lead added to the aqueous solution results in the formation of an opaque white jelly. Iodine does not produce any colour in solutions of gum arabic. Nitric acid converts them into mucic and oxalic acids, while boiling with sulphuric acid converts them into dextrine and sugar.

Gum arabic consists essentially of arabine, a compound of arabic acid with lime; besides this compound, gum contains traces of sugar, dextrine, colouring matter, tannin, and mineral matter.

Gum Tragacanth.—This gum is an exudation from various species of *Astragalus*, of which the most common is *A. gummifera*, growing in Lebanon, Syria, Central Asia Minor, Judea, and Armenia. Other species grown in Asia Minor, Judea, Syria, and Persia also yield gum tragacanth, which comes into commerce principally through Baghdad. Gum tragacanth occurs in two forms—(1) leaf gum, in stripes of about $\frac{1}{2}$ to $\frac{3}{4}$ inch wide and 2 to 3 inches long; (2) "vermicelli" gum in long round pieces. It is of a dull greyish colour, without odour or taste. Placed in cold water it does not dissolve, but swells up into a gelatinous mass, which, when boiled for some considerable time, gradually passes into a kind of solution forming a very jelly-like

fluid. It is readily soluble in alkaline liquids, but not in alcohol. It consists essentially of a compound known as bassorine, which is insoluble in water and alcohol. Besides this there is generally a small quantity of ordinary arabine in soluble gum. Gum tragacanth, owing to its dull appearance, is not used in varnish-making, but as a thickener in calico printing, and for a few other purposes.

Besides these two gums, other kinds of gums are occasionally met with in small qnantities in the London market. Some resemble gum arabic in their properties, and can be used for the same purposes; others resemble gum tragacanth; while some, such as kuteera gum of India, appear to contain both soluble and insoluble gums.

Dextrine or **British Gum.**—This product sometimes occurs in water varnishes. It is prepared by acting on starch, either by heating alone or by heating with a small quantity of acid; the former method is most commonly used in England, and gives the best dextrine; the acid method is the one by which German dextrine is mostly prepared. Dextrine comes into commerce as a powder varying in colour from a pale yellow "white" to a dark brownish - yellow "yellow" dextrine; intermediate varieties being known as "canary." Pure dextrine is quite white, tasteless, and free from odour; the commercial varieties have a sweetish taste and a slight odour. Pure dextrine is quite soluble in water; the solution reduces Fehling's solution and gives a brownish colour with iodine. The solubility of the commercial dextrines varies considerably; some are quite soluble, others are only partly soluble, as they still contain some unchanged starch. These solutions reduce Fehling's solution, and often give a blue colour with iodine. The solutions have more or less adhesive properties; hence dextrine is largely used for adhesive purposes as a substitute for gum arabic. Dextrine dries with a fair amount of gloss or lustre; hence it is used in making water varnishes. There is a considerable difference in the commercial varieties of dextrine in regard to both their adhesive and lustreing properties; some, while giving a thick mucilage, have little adhesive property, and others dry with little gloss. On boiling with water, dextrine gradually loses its adhesive properties, which change is hastened by the addition of small quantities of acid; this is due to the transformation of the dextrine into sugar.

RESINS.—This is by far the most important group of varnish materials, for on these bodies the lustre and lasting properties of the varnishes depend. They are all of natural

origin, being exudations from various species of trees. They are very numerous. Some are used almost exclusively for varnish-making, others are also used for other purposes, while some resins are not used for varnish-making, but find use in other directions.

As a class, they are distinguished by being more or less hard, friable or brittle, lustrous, generally clear and transparent, although some are slightly opaque, insoluble in water, and soluble in alcohol, ether, benzol, and other solvents of a similar character to a greater or less extent. In composition they are very complex, being mixtures of bodies having acid properties. A few only of these bodies have been isolated and their chemical characters investigated; they are rich in carbon, poor in oxygen, and contain no nitrogen. They are more or less combustible, usually burning with a smoky flame. They are usually devoid of colour, which is a valuable feature for varnish-making, although some are coloured. As a rule, they are free from odour, but some possess fragrant and characteristic odours.

Classification of Resins.—The resins can be classed into various groups. Cooke classes them into three divisions—1st, Resins; 2nd, Gum resins; and 3d, Oleo-resins. The resins possess the properties enumerated above, and will be again referred to below. The gum resins contain a little gum as well as resin in their composition; very few are used for varnish-making. The oleo-resins consist essentially of a mixture of resin with a liquid oil which imparts to them a viscid character; they are useful bodies, although few find their way into varnishes. The resins can be divided into two groups, hard or copalline, soft or elemi resins.

Character of Resins.—Some of these have been pointed out above in a general manner, but it is advisable to deal with them in a more detailed manner. The most important characters of resins are from appearance, colour, hardness, specific gravity, and solubility.

Form.—Most resins occur in the form of knotty masses, some in the form of drops, and others in that of cylindrical pieces. The resin flows out of the tree in the form of drops; if the resin solidifies quickly it keeps this form, as, for example, mastic; if the process of solidification is slow, then the resin tends to form into tears or cylindrical pieces, as, for example, sandarac; if, again, the process goes on slower and the resin collects on the tree or drops on to the ground, or forms into knotty masses of various sizes and shapes, as, for example,

copal, animi, dammar, &c. Some resins come into the market artificially shaped, as, for instance, gamboge in cylinders, shellac in thin plates, dragon's blood in thin sticks or powder, and benzoin and elemi in blocks.

Appearance.—The appearance of many of the resins is characteristic. Animi is clear and transparent and has a peculiar rough surface, which, from its appearance, is known as the goose skin; benzoin, elemi, and some others have more or less an agglomerate appearance, as if made up of two or three kinds of gum; such a structure is called, by mineralogists, *amygdaloidal.* Animi and copal have a very lustrous appearance; elemi, benzoin, &c., are more waxy; kauri partakes somewhat of both, and has a semi-lustrous appearance; animi, copal, sandarac, dammar, and kauri are more or less crystalline; while elemi and benzoin are amorphous in appearance.

Colour.—Resins vary very much in colour. Accroides or xanthorrea is deep yellow, copal mostly of a brownish-yellow, and dragon's blood of a red colour, dammar is almost colourless, shellac has an orange colour, elemi is usually of a greyish tint, ammoniacum of a brown, and asphaltum a deep brown, almost approaching a black; the large majority of the resins are of a pale brownish colour. The colour of resins is a most important feature in varnish-making, inasmuch as any colour they may possess affects the colour of the varnish made from them; the difference between two varnishes sometimes arises from the quality of the resin used, not from the kind of resin or other materials, but from the method of preparation. In the best varnish the resin used is of the best quality and has the purest colour, while inferior varnish made with an inferior quality of resin the colour of which is rather darker. In copal varnishes, for instance, where there are so many varieties of copal, so far as regards colour (ranging from almost colourless to pale brown), the purest copals only are used for pale copal varnishes, the oak varnishes being made from the darker coloured copals.

Hardness and Fusibility.—In these two features, hardness and fusibility, there is a wide range of difference between the various resins. Some, such as the hard copals, amber, and animi, are very hard and difficult to melt; these resins are the very best of the varnish resins, giving the finest and most durable kinds of varnishes, which are, however, the most difficult to make. Some resins, such as elemi, are so soft as to easily bend between the fingers, and will melt or become softened by the heat of the hands; such resins do not give durable varnishes,

and they are only used to tone down the hardness and brittleness of other resins. Some resins, as animi and amber, are hard and difficult to break up; others again, as accroides, rosin, &c., are brittle and easily reduced to a powder; the former class yield durable varnishes, which, when applied to a surface, will stand a good deal of wear and tear; the latter class make varnishes which do not stand much wear and tear. The resins vary in the appearance of the fracture when broken; some exhibit a conchoidal or shell-like fracture, others a ragged appearance, some a powdery fracture, and some a smooth fracture. The particular kind of fracture of each resin will be described when each resin is described in detail.

Specific Gravity.—Resins are all heavier than water; some, as copal, amber, and sandarac, are only slightly heavier; others, as benzoin, guaiacum, and shellac, much heavier. The specific gravity of each particular resin does not vary very much, so that this is a distinguishing feature which may be taken advantage of in making an examination of resins. The following table gives the specific gravity of most of the varnish resins:—

Animi, 1·043 to 1·067.
Amber, 1·047 to 1·094.
Benzoin, Siam, 1·135.
,, Penang, 1·145 to 1·155.
,, Borneo, 1·165 to 1·170.
Copal, Sierra Leone, 1·054.
,, Angola, 1·064.
,, Pebble, 1·055.
,, Manila, 1·063.
Dammar, 1·055 (Batavian).
,, 1·062 to 1·123 (Singapore).
Thus, 1·042.
Dragon's blood, 1·200.
Elemi, 1·019.
Gamboge, 1·025.
Guaiacum, 1·236 to 1·237.
Kauri, 1·050.
Mastic, 1·056 to 1·06.
Sandarac, 1·038 to 1·044.
Shellac, 1·113 to 1·214.
Accroides, 1·197.
Locust, British Guiana, 1·030.
Rosin, 1·044 to 1·100.

Solubility.—This is a very important property of resins, and influences to a very great extent the use to which they are put. There is a great deal of difference between the resins in regard to their solubility in various media; some, as animi and copal, are insoluble in any solvent, and before they can be made into varnishes have to be fused by heat; others, as shellac, sandarac, Manila copal, and rosin, are soluble in alcohol, ether, and benzol, and are easily made into varnishes. Other resins are not so easily soluble, as, for instance, dammar, mastic, &c. Acetone, ether, and benzol are the best solvents for resins; they will act more or less on all the resins of the last two classes. Petroleum spirit is a poor solvent for the resins, only rosin and dammar being dissolved by it.

THE VARNISH RESINS.

The general properties of the resins used in the preparation of varnishes having already been given, a few notes on the principal ones, giving their origin and characteristics, will be of service to the student.

Animi.—This important varnish resin is found chiefly in a fossil condition in the Island of Zanzibar, and on the mainland of that part of East Africa immediately opposite to it. The natives dig it up out of the ground during the rainy season. As dug up the resin is covered with a reddish earthy crust, which is chipped off it before it is sent to market or used in varnish-making. Animi comes in the form of hard, clear, transparent masses, the outer surface of which has small round markings, not unlike those on the skin of the goose. Sometimes remains of flies and other insects are found imbedded in the mass of resin. It is very hard, and breaks with a conchoidal fracture. The specific gravity is about 1·062.

It is not soluble in any of the ordinary solvents, chloroform, ether, benzol, or turpentine; long-continued digestion may cause a portion of the resin to pass into solution, but it is not completely soluble in any. When heated to from 240° to 250° C. (450° to 465° F.) it melts to a thin liquid, and gives off volatile vapours. After cooling down, melted animi is soluble in hot linseed oil, and in turpentine, benzol, petroleum spirit, but not in alcohol.

Animi is used in making the best quality of carriage and cabinet oil varnishes, giving a varnish remarkable for its lustre and durability.

Copal.—This gum is a fossil resin found over a large extent of the West Coast of Africa; the principal supply comes from Sierra Leone, but a good deal comes from the Gaboon, Angola, Accra, Loango, and other places. Various qualities of these West African copals, dependent on the size of the pieces, colour, clearness, &c., are recognised in the market, but all can be used in making the same kinds of varnish.

In its general properties copal resembles animi; it is scarcely so hard, nor does it yield varnishes so lustrous or durable, but as a varnish gum it is far superior to all other resins except animi.

The specific gravity of copal varies from 1·054 to 1·064; it is quite insoluble in ether, turpentine, benzol, and similar solvents. It melts at 400° F. (205° C.), and, after melting, the resin becomes soluble in hot linseed oil, turpentine, benzol, and petroleum spirit.

The term "copal" has been applied to other resins which come from South America and Asia, but these only resemble copal in their outward appearance, and differ considerably in their properties and uses. The term "copal" should be restricted entirely to that found on the West Coast of Africa.

Kauri.—This is a fossil gum found in various districts of New Zealand; it is fairly plentiful, and is often found in large blocks. Many grades are recognised in the market, these grades being based on differences of colour, clearness, &c.

The resin is supposed to be the product of a species of pine tree, the *Dammara Australis;* this tree must have been very prolific at one time, but it is now rather scarce. The living tree yields a resin, but this is not of so good a quality as that found in a fossil condition, although it is collected and sold for varnish-making.

Kauri is usually a pale amber to pale brown in colour, sometimes clear and transparent, at other times streaky and opaque. It is hard and rather brittle, breaking with a conchoidal fracture, and when fresh the resin has a pleasant fragrant odour and an aromatic taste. The marked odour and taste distinguish kauri from copal and animi.

Kauri has a specific gravity of 1·050, varying a little in different samples. It melts fairly easily at 360° to 400° F. It is not soluble in alcohol, ether, benzol, or turpentine, although by long digestion with these solvents a portion passes into solution. Long digestion with caustic soda brings about solution.

Kauri is largely used in making oil varnishes; these are not of so good a quality as copal varnishes; when exposed to the weather they are apt to become powdery. For indoor woodwork they are well adapted, and wear well.

Demerara Copal.—In British Guiana and other places in the northern portion of South America, a resin is found in a fossil condition which is supposed to have been derived from the locust tree, *Hymenæa courbarii.* This resin resembles copal in appearance, but it is somewhat softer. It has a specific gravity of 1·030 and melts at 450° F. It is more soluble than copal or animi; it is soluble in ether, and while not completely soluble in petroleum spirit and alcohol, these solvents act more freely on it than on copal. It is sometimes called locust gum.

When melted, it loses more volatile matter than copal, but it does not yield varnishes of the same quality.

Sandarac.—This resin is also known as gum juniper. It is obtained from the Alerce tree, *Callitris quadrivalvis,* which

grows in North Africa. The resin is collected direct from the tree.

It comes into commerce in the form of short cylindrical tears which are often agglomerated together, these have a yellowish-white colour, is hard and brittle, and melts at 300° F. The specific gravity is 1·038.

Sandarac is readily soluble in alcohol and ether, and partially so in benzol, petroleum spirit, and turpentine.

It is chiefly used for making spirit varnishes, either alone or in conjunction with shellac and other gums. It has been used in making oil varnishes to a small extent.

Dammar.—This is the name given to several resins which come from the Straits Settlements, Siam, and other places in Eastern Asia. There is not much difference between them in their properties, and all may be used for making the same kind of varnishes. Singapore dammar is obtained from the Amboyna pine, *Dammara orientalis*, a very common tree in the Straits Settlements. This is perhaps the variety best entitled to the name of dammar.

It comes into commerce in the form of nodules varying in size from ½ inch to 2 inches; the outside is often covered with a powdery crust; the substance of the resin is very clear and transparent. It is generally free from colour, but at the most the tint is rarely deeper than straw tint.

It is brittle and can be readily powdered. The specific gravity is 1·062. It melts at about 260° F. It is soluble in turpentine, ether, benzol, chloroform, and in hot linseed oil, but is only partially soluble in alcohol and amyl alcohol. Dammar is usually made into a varnish by dissolving in turpentine; such varnish is largely used for covering pictures and paper. It is rather lustrous, but somewhat friable in character. Melted and mixed with hot linseed oil and turpentine it gives a lustrous durable varnish.

From the *Hopea odorata* growing in Burmah, and the *Hopea micrantha* which grows in the Malay States, is obtained dammar differing but slightly from the dammar just described and which can be used for the same purposes.

The Sal tree, *Shorea robusta*, of the Himalayas yields a species of dammar which differs slightly as regards solubility from the other dammars. This variety of dammar is not often seen in Europe.

Mastic.—The Lentisc tree, *Pistachia lentiscus*, which grows on the coasts of the Mediterranean Sea, yields the gum or resin known as mastic. It comes into commerce in this

country chiefly in the form of tears, called "small" mastic; it also forms cakes of various sizes known as "cake" and "large" mastic. In some countries of the Eastern Mediterranean it is used as a chewing gum.

Mastic tears vary in size from $\frac{1}{4}$ to $\frac{1}{2}$ inch, of a pale yellow tint, sometimes with a powdery crust, while at others it is clear and transparent. Mastic is brittle and breaks with a glassy fracture. In some respects it resembles sandarac, from which it is distinguished by its becoming soft in the mouth and having a balsamic odour and taste. It has a specific gravity of 1·056, softens below 100° F., and melts at 220° F.

It is easily soluble in turpentine, alcohol, chloroform, amyl alcohol, and acetone, but not in petroleum spirit. It is used in making spirit varnishes of all kinds; what is called mastic varnish is a mixture of mastic and turpentine and this is often used for varnishing pictures. It gives clear, transparent, nearly colourless varnishes, drying with a lustrous and fairly durable coat.

Manila Copal.—Under this name there is imported from the Philippine Isles, through the Port of Manila, resins gathered from various trees growing in these islands. There are two varieties of Manila copal to be distinguished, hard and soft, the latter is more soluble in character than the former.

Manila copal comes in the form of pebble-like pieces, of a brownish-yellow colour, having a specific gravity of 1·063. It melts at 230° to 250° F. It is partially soluble in petroleum spirit, the residue forming a gelatinous mass. It is soluble in ether. Alcohol forms a somewhat turbid solution. It is only partially soluble in benzol, chloroform, and turpentine. After being melted Manila copal is readily soluble in all the above solvents. The soft copal is rather more soluble than the "hard" copal.

Manila copal is used along with shellac, sandarac, &c., for making spirit varnishes, imparting some degree of elasticity to the varnish but not adding any lustre.

To call this resin a "copal" is to give it a misleading name, for it cannot be used in making an oil varnish like a true copal varnish.

Shellac.—The most important resin used in the preparation of spirit varnishes is shellac.

Lac is an incrustation which is found on many trees growing in India. It is not a direct product of the tree, but is caused by the attacks of the lac insect, the *Coccus lacca.* The females of this insect are wingless, they puncture the bark of the tree,

and from the sap which exudes, form cells in which they live and lay their eggs, after which they die. The young insects, when they develop, puncture the lac and come forth ready to propagate their kind. A tree gives nourishment to a large quantity of insects, but a tree much infested loses its vitality and soon dies. The twigs, with the incrustation on them, are collected and sold under the name of stick lac. From this the various kinds of lac products are produced in the following manner:—

The *Stick Lac* is placed on tables and the lac separated from the wood by passing a roller over it. The wood is thrown away. The lac is thrown into warm water in which it is kneaded; this causes some colouring matter to separate out of the lac, together with other impurities. The crude lac so obtained is called *seed lac.*

To obtain shellac the seed lac is first boiled up with water, to separate out as much colouring matter as possible; it is then dried and put into bags which are held in front of a hot fire; the lac melts and drains out, and drops on to a wooden cylinder which is kept revolving and wet with water. This causes the lac to form very thin flakes which are then known as *shellac.*

Several grades of shellac are recognised in the market varying in thickness, colour, &c.; the best is called "orange shellac."

Button Lac is made in the same way as shellac, only it is formed into thick circular discs, like buttons; hence its name. *Garnet lac* is similar but darker in colour. Both these varieties of lac may be used in making varnishes in the same way as shellac, but these varnishes are deeper in colour than are similar varnishes made from orange shellac.

Lac comes into commerce in three forms—shellac, in thin flakes, of an orange colour varying a little in shade and transparency; button lac, in irregularly-shaped flat pieces of a dark ruby colour; and garnet lac. It is rather brittle and easily broken up into small pieces. Occasionally it is artificially coloured with orpiment or mixed with rosin, but such adulterations are rare.

Lac is incompletely or only partially soluble in alcohol or methylated spirit, forming a turbid brownish-orange solution, which is largely sold as French polish and varnish for cabinet and other work; it is soluble in amyl alcohol.

Lac is only partially soluble in ether, chloroform, and turpentine, while it is insoluble in petroleum spirit. It is soluble in solutions of caustic potash, and of caustic soda to dark red solutions. In borax solutions and in weak ammonia it

is also soluble, and such solutions are sometimes used as water varnishes. One point of interest in the solubility of shellac in such alkaline liquors is that the colouring matter is first dissolved away from the resin proper, leaving the latter of a pale colour; this property is taken advantage of in preparing white shellac. Chlorine passed through alkaline solutions of lac throws down the resin free from colour. Lac has a specific gravity of 1·113 to 1·214, the darker varieties being the heavier.

Crude stick lac freed from woody matter contains 66·67 per cent. of resin, 6 per cent. of wax, 6 per cent. of gluten, and 10·8 per cent. of colouring matter. From shellac five distinct resins have been separated—(1) resin soluble in alcohol and ether; (2) resin soluble in alcohol, but insoluble in ether; (3) resin slightly soluble in alcohol; (4) a crystallisable resin; and (5) an uncrystallisable resin. These constitute about 90 per cent. of the shellac. There are in addition (6) fatty matter, (7) wax, (8) gum, and (9) colouring matter.

Bleached or *White Shellac.*—Shellac may be bleached in two or three ways. One method is to boil ordinary shellac in a weak solution of carbonate of potash, and, when dissolved, passing a current of chlorine through it; the lac precipitated is collected, melted under water, and then, while soft, pulled so as to give it a fibrous satiny appearance. Another method is to boil the shellac in a weak solution of potash, and, while melted, pulling and working together until the desired whiteness has been attained. Then the shellac is re-melted and re-pulled in clean warm water. White shellac is sold in the form of long cylindrical pieces having a fibrous satiny appearance. It is used for making white varnishes and for other purposes where a white shellac is required; as it is sold in a rather wet condition it is necessary to dry it before using it. White shellac deteriorates on keeping, becoming insoluble in alcohol and borax.

Manila Elemi.—This comes from the Philippine Islands, and is the product of a tree known as *Canarium commune* to botanists, which principally grows in the island of Luzon; the supply is sent through Manila. This variety of elemi is white, when quite pure and of good quality, although some samples have a grey appearance, and others appear to be composed of two or three sorts of resins. The resin is soft and has a granular appearance; when exposed to the air for some time it becomes hard, owing to the evaporation of the volatile oil present in freshly-gathered elemi. The odour is slightly turpentiney. When distilled this elemi yields about 10 per cent. of an oil

resembling turpentine in its composition. Elemi begins to soften at about 75° to 80° C., and is quite liquid at 120° C. It is soluble in alcohol and in most other solvents. It is used in varnishes to give elasticity or toughness.

Benzoin.—Gum benzoin or gum benjamin is a balsamic resin which exudes from the tree *Styrax benzoin*, a native of Sumatra, Java, Borneo, Siam, Laos, and other places in the same region. The commercial product comes principally from Siam and Sumatra. The Malays know it by the name of "kaminian." In the coast regions of North and East Sumatra it is cultivated from seed. In about seven years it obtains a diameter of 6 to 8 inches and is then ready to cut. The natives make incisions in the tree and the resin exudes from them very freely, each tree yielding about 3 lbs. annually; for the first three years the product is of first-class quality, of a yellowish-white colour and soft, with a fragrant odour; after the third year the product is darker in colour, harder, and not so fragrant; after about nine years it is not worth collecting. In the interior regions the resin is collected from wild trees.

The benzoin imported into England mainly comes from Siam and Sumatra. The two varieties differ slightly in appearance and properties.

Siam benzoin occurs either in agglutinated, flattened, somewhat opaque, milk-white tears, or in large agglomerations of white masses distributed through an amber-coloured, rather translucent matrix. It is brittle, and has a strong characteristic vanilla-like odour. It is readily softened by heat; it is quite soft at 75° C. and fluid at 100° C.

Sumatra benzoin is rather greyer, and is in the form of an agglomerate mass with white tears distributed through a darker translucent matrix. Its odour is not so strong as that of Siam benzoin and it does not melt so easily.

Ludz states that it contains about 12 to 15 per cent. of ligneous matter. The resin contains cinnamate of benzoresinol, 5 per cent.; cinnamate of resinotannol, 64 per cent.; cinnamic acid, 30 per cent.; with small quantities of vanillin and benzoic acid. It is, therefore, a source for the preparation of cinnamic acid, while the benzoresinol and the resinotannol can be employed in making picric acid.

Penang benzoin contains about 10 per cent. ligneous matter, much benzoic acid, and no cinnamic acid.

Palembang benzoin contains 7 to 8 per cent. of impurities, benzoic acid, and no cinnamic acid.

Benzoin has a peculiar fragrant odour, and is slightly heavier

than water, its specific gravity being about 1·135 to 1·175. It melts at a gentle heat, and gives off white vapours of benzoic acid with a small quantity of volatile oil. Alcohol dissolves most of it, ether rather less, but turpentine and petroleum spirit dissolve very little. Treated with sulphuric acid benzoin or an alcoholic solution turns red, while with ferric chloride a green colour is produced.

Benzoin finds a small use in varnishes, chiefly on account of the odour which it imparts to the varnish; it is also used in making perfumes, incense, &c.

Rosin or Colophony.—The name of this body is spelled indifferently, rosin or resin; the former is more in accordance with the pronunciation of it and will be adopted here; the latter is liable to confusion with the generic name for the group of resins. Colophony is of French origin and is rarely used. Rosin is obtained in the distillation of turpentine from gum thus, and is left behind in the still after the turpentine has come over; the melted rosin is run from the stills into moulds or barrels to cool. Rosin comes into the market in the form of large pieces, generally homogeneous, varying in colour and transparency; the best quality is known as "window glass" rosin, and is a pale amber in colour, perfectly clear and transparent, "common" rosin is much darker in colour, but is still homogeneous, clear and transparent; "black" rosin is very dark, almost approaching a black, and opaque. These varieties are dependent upon the quality of the original resin from which the rosin has been made; the so-called "virgin" resin gives the best rosin, while the resin collected later in the season gives common rosin, and the scrapings of the resin from the bark, &c., give black rosin. Rosin is slightly heavier than water, its specific gravity being 1·044 to 1·100; it easily melts; at about 177° F. it softens, and at 212° F. it is quite fluid; "window glass" rosin forms a clear, limpid, yellow liquid. It is insoluble in water, is soluble in about eight times its weight of alcohol, in benzol, amyl alcohol, coal-tar naphtha, and acetone in almost any proportion; it is also soluble in turpentine, ether, and most oils. It is also soluble in boiling solutions of the alkaline carbonates or hydroxides, becoming hydrolised and taking up the elements of water to form abietic acid, with which the alkalies combine to form the rosin soaps so largely employed in the soap industry. Rosin is a mixture of two acid bodies, pinic and sylvic acids, which are isomeric and have the formula $C_{20}H_{30}O_2$. Some authorities consider that the composition of rosin is not that of a true acid, but of an anhy-

dride, abietic anhydride, which will take up water to form abietic acid.

When distilled, rosin yields a small quantity of acid water, spirit, a heavy oil, and a residue of pitch. It is used in making common oil varnishes, in making some cheap spirit varnishes, and in naphtha varnishes. By itself it leaves rather a hard, brittle, and lustrous coat, but tempered with some oil or soft resin it makes a durable varnish, not, of course, approaching the copals or kauri in this quality.

A solution in hot alcohol deposits crystals of sylvic acid on cooling. Nitric acid converts rosin into terebic acid, $HC_7H_9O_4$, which is soluble in water.

ASPHALTUM.—Asphaltum or native bitumen is used in the varnish manufacture in the production of black varnishes, blacks, japans, &c. It was originally obtained from the shores of the Dead Sea, and this variety is especially designated bitumen of Judea and Egyptian asphaltum, but it is imported from other places, Altona in Albania, Coxitambo in South America, and Barbados, while there is an almost inexhaustible supply in the great lake of Trinidad. Asphaltum, when pure, is a blackish-brown solid, breaking with a conchoidal fracture, the surfaces being bright and lustrous. At 100° C. (212° F.) it melts to a black somewhat smoky flame. In water and alcohol it is insoluble. It dissolves readily in coal-tar naphtha, but not so readily in turpentine. Its specific gravity varies from 1·00 to 1·20.

When used alone, simply dissolved in naphtha or turpentine, it dries with a gloss, with, however, a very brittle coat that in time begins to crack very much. On this account asphaltum, formerly much used by artists, has of late years been abandoned for oil painting.

In making japans and black varnishes its brittleness has to be overcome by the use of oil and other gums. Asphaltum is generally considered to be a product of the decomposition of animal and vegetable organic matter.

SPIRIT VARNISHES.

Spirit varnishes are made by dissolving such resinous matters as shellac, mastic, sandarac, elemi, benzoin, dammar, resin, &c., in methylated spirit, benzol, turpentine, or coal-tar naphtha. As a class they are easily made, all that it is necessary to do is to mix the resin with the solvent in a suitable vessel, a glass bottle, if only a small quantity is being made, a barrel in

the case of large quantities; shaking or stirring the mixture occasionally to promote the solution of the resin in the spirit. Heat is not necessary nor should it be applied, for it invariably means loss of spirit or solvent.

The following are a few typical spirit varnishes :—

French Polish.—Methylated spirit, 1 gallon; shellac, 2 lbs.; gum benzoin, 4 ozs.

Shellac Varnish.—Methylated spirit, 1 gallon; shellac, $1\frac{1}{2}$ lbs. This practically forms the basis of a large number of spirit varnishes passing under a variety of names and produced by taking the above and adding various colouring matters, such as Bismarck brown, dragon's blood, nigrosine, spirit ebony, &c., and other resinous matters.

Brown Hard Spirit Varnish.—Methylated spirit, 1 gallon; sandarac, 1 lb.; shellac, $\frac{1}{2}$ lb.; gum elemi, 4 ozs.; Venice turpentine, 4 ozs.

White Hard Spirit Varnish.—Methylated spirit, 1 gallon; gum thus, 1 lb.; gum sandarac, $2\frac{1}{2}$ lbs.

Mastic Varnish.—Turpentine, 1 gallon; gum mastic, 4 lbs.

Dammar Varnish.—Turpentine, 1 gallon; gum dammar, 3 lbs.

Paper Varnish.—Methylated spirit, 1 gallon; gum sandarac, 2 lbs.; gum mastic, 1 lb.; gum elemi, 2 ozs.

Collodion Varnish.—Gun cotton, 1 oz.; amyl alcohol, 1 gallon; amyl acetate, $\frac{1}{2}$ gallon. This makes a fine transparent varnish, very useful for coating gilded articles.

For further information and formulæ reference can be made to the *Manual of Painters' Colours, Oils, and Varnishes.*

Spirit varnishes dry very quickly, in from ten to thirty minutes according to the solvent used.

Lacquers are spirit varnishes made weaker than ordinary varnishes and coloured with some coal-tar dye, &c. They are used for coating brass and other metallic articles.

OIL VARNISHES.

These varnishes are very largely used, especially for woodwork of all kinds, and form the most durable varnishes known; they are slow in drying, taking from twelve to twenty-four hours, but dry with a fine, uniform, and lustrous coat. They are most difficult to make. The process is given in detail in the author's *Manual of Painters' Colours*, and to this reference should be made. The following outline of the process is, however, given :—

These varnishes are made from such resins as copal, animi, amber, kauri, rosin, &c., which, as a class, can practically only be made into varnishes by this process.

The gum or resin is melted over a furnace in a copper pot, the "gum pot" as it is called, with constant stirring; great care must be taken in this operation to have the whole of the gum melted, but that the heat be not too great. Some decomposition of the gum occurs, and there is a loss of weight ranging from 15 to 25 per cent. of the weight of the gum.

Next linseed oil of good quality is heated to 500° F., and the hot oil is poured into the melted gum, the usual proportions being 8016 gallons of gum to 35 gallons of oil. By stirring, the two are well mixed together, and the mixture is kept at from 400° to 500° F. for some hours, until a little taken between the finger and the thumb can be drawn into long strings.

The mixture of oil and gum is now allowed to cool down to about 250° F., and a quantity of turpentine added to make it fluid and of the right consistence.

After being thus thinned down, the varnish mixture is stored in large tanks for some months to allow the ingredients to become properly amalgamated together and to clarify, all solid particles settling down to the bottom of the tank.

The student can imitate this process on a small scale by placing 20 grammes of gum kauri at the bottom of a large test tube, 7 inches by $1\frac{1}{4}$ inches, and heating over a Bunsen burner. After the gum has become liquefied the heating should be continued for about ten minutes. At the same time 80 c.c. of oil are heated to 400° F., and, while hot, are poured into the melted gum; the mixture is now kept hot until a portion taken out strings well. The whole mass is allowed to cool down, and 40 c.c. of turpentine are added, with constant stirring; when the mixture is made, the varnish is practically finished.

The following are a few typical oil varnishes :—

Coach Body Varnish.—80 lbs. of gum animi, 20 gallons of linseed oil, and 35 gallons of turpentine.

Carriage Varnish.—80 lbs. of gum copal, 25 gallons of linseed oil, 2 lbs. of litharge, and 55 gallons of turpentine.

Hard Carriage Varnish.—40 lbs. of gum kauri, 20 gallons of linseed oil, 2 lbs. of sugar of lead, and 35 gallons of turpentine.

Church Oak Varnish.—80 lbs. of gum kauri, 30 gallons of oil, and 35 gallons of turpentine.

Varying grades of the above varnishes are made by using poor or good grades of the gum, and by making slight variations in the process of making.

Gold Size.—80 lbs. of gum copal, 96 gallons of linseed oil, 50 lbs. of red lead, 50 lbs. of litharge, and 240 gallons of turpentine.

Black Japan.—40 lbs. of asphalt, 32 gallons of oil, 14 lbs. of litharge, 14 lbs. of red lead, and 120 gallons of turpentine.

Brunswick Black.—45 lbs. of asphalt, 6 gallons of oil, 6 lbs. of litharge, and 25 gallons of turpentine.

Attempts have been made to manufacture oil varnishes by other processes than the one given, partly with the idea of avoiding the loss of weight which occurs when the gum or resin is melted; thus, for example, the gum has been melted under pressure in a closed vessel made sufficiently strong so as to withstand considerable pressure; in this case the oil and spirit produced during the decomposition of the gum are retained, and enter into the composition of the varnish. There are strong elements of doubt as to the practicability of the process and as to the quality of the varnish produced, while there is a greater element of risk attendant on the carrying out of this process.

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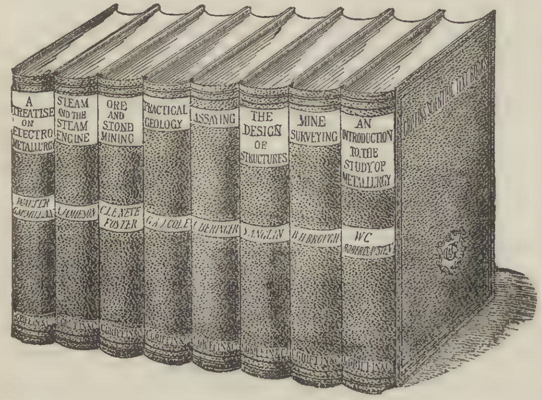

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